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PYROLYSIS OF HIGH BTU NATURAL GASES

by

Wayne A. Platt

EDMONTON, ALBERTA

August 29, 1957.

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PYROLYSIS OF HIGH BTU NATURAL GASES

A DISSERTATION
SUBMITTED TO THE SCHOOL OF GRADUATE STUDIES
IN PARTIAL FULFILLIMENT OF THE REQUIREMENTS FOR THE
DEGREE OF MASTER OF SCIENCE

FACULTY OF ENGINEERING
DEPARTMENT OF CHEMICAL AND PETROLEUM ENGINEERING

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ACKNOWLEDGEMENT

The author would like to express his sincere thanks to the following for their assistance in this work.

To Dr. G. W. Govier and the other members of the Department of Chemical and Petroleum Engineering of the University of Alberta.

To Dr. D. Quon whose suggestions and constructive criticism as director of the project aided greatly in the carrying out of this investigation.

To the Research Council of Alberta for their sponsorship of the project and the financial assistance which enabled the author to carry out the work. The Research Council also carried out the analysis of the gas samples and prepared the final drawings accompanying this report.

To all the others whose assistance has aided in the completion of this study.

ABSTRACT

The pyrolysis of normal butane diluted by a lean natural gas and of a rich natural gas containing significant amounts of ethane, propane, and butane was investigated at temperatures in the order of 2000°F in a continuous tubular reactor. The effects of temperature, space velocity and hydrocarbon concentration in the feed gas on the product yield were investigated.

The main decomposition products were found to be methane, ethylene, acetylene, carbon and hydrogen. Small amounts of propylene were formed at the less severe pyrolysis conditions. Of these ethylene and acetylene are of commercial interest.

Ethylene yield was found to pass through a maximum with respect to space velocity. The acetylene yield decreased with increasing space velocity over the range investigated. The ratio of ethylene to acetylene increased with the carbon number of the feed.

A process for production of acetylene and ethylene by pyrolysis of a rich natural gas has commercial possibilities, if a suitable method of supplying the large energy requirements of the process at a high temperature level can be devised.

TABLE OF CONTENTS

Abstract

Acknowledgement

List of Illustrations

Introduction 1

Theoretical Background 3

- a) Thermodynamics 3
- b) Kinetics and Mechanism 6
- c) Commercial Processes 7
  - 1. Schoch Process 7
  - 2. Sacchsse Process 7
  - 3. Wulff Process 7

Equipment and Procedure 9

Results 12

Discussion and Conclusions 15

Bibliography 22

Appendix - Calculations and Results 23

- a) Material Balance Calculations 23
- b) Space Velocity Calculation 25
- c) Calculation of C_2H_4 - C_2H_4 Equilibrium 30
- d) Calculation of CH_4 - C_2H_2 Equilibrium 31
- e) Gas Temperature Estimation from Heat Transfer Considerations 35

LIST OF ILLUSTRATIONS

1. Acetylene-Ethylene Equilibrium Ratios 5 (a)

2. Acetylene-Methane Equilibrium Ratios 5 (a)

3. Pyrolysis of Normal Butane at 2000°F and 50 mm Hg. 6 (a)

4. Product Distribution for the Decomposition of Propane by the Hasche Process 8 (a)

5. Schematic Diagram of Reaction System 9 (a)

6. Reactor Furnace 10 (a)

7. Reactor Furnace 10 (b)

8. Circular Reactor Tube 10 (c)

9. Annular Reactor Tube 10 (d)

10. Control Panel 11 (a)

11. Product Distribution for Pyrolysis of Butane with Natural Gas Dilution

    Circular Reactor Tube - Space Velocity = 15 sec^{-1} 13 (a)

12. Product Distribution for Pyrolysis of Butane with Natural Gas Dilution

    Circular Reactor Tube - Space Velocity = 25 sec^{-1} 13 (b)

13. Product Distribution for Pyrolysis of Butane with Natural Gas Dilution

    Circular Reactor Tube - Space Velocity = 35 sec^{-1} 13 (c)

14. Product Distribution for Pyrolysis of Butane with Natural Gas Dilution

    Annular Reactor Tube - Space Velocity = 15 sec^{-1} 13 (d)

15. Product Distribution for Pyrolysis of Butane with Natural Gas Dilution

    Annular Reactor Tube - Space Velocity = 25 sec^{-1} 13 (e)

16. Product Distribution for Pyrolysis of Butane with Natural Gas Dilution

Annular Reactor Tube - Space Velocity = 35 sec^{-1} 13 (f)

17. Product Distribution for Rich Natural Gas Pyrolysis 13 (g)

18. Ethylene Yields in Circular Reactor Tube 14 (a)

19. Acetylene Yields in Circular Reactor Tube 14 (a)

20. Ethylene Yields in Annular Reactor Tube 14 (a)

21. Acetylene Yields in Annular Reactor Tube 14 (a)

22. Ethylene Yields Showing Effect of Space Velocity in Circular Reactor Tube 14 (b)

23. Acetylene Yields Showing Effect of Space Velocity in Circular Reactor Tube 14 (b)

24. Ethylene Yields Showing Effect of Space Velocity in Annular Reactor Tube 14 (b)

25. Acetylene Yields Showing Effect of Space Velocity in Annular Reactor Tube 14 (b)

26. Heat Load - Temperature Relationships for Circular Reactor Tube 15 (a)

27. Heat Load - Temperature Relationships for Annular Reactor Tube 15 (b)

TABULATIONS

1. Free Energy Changes for Decomposition Reactions 3
2. K_p Values for Decomposition Reactions 4
3. Heats of Reaction for Decomposition Reactions 5
4. Effect of Reactor Tube Geometry on Heat Transfer 19

APPENDIX

1. Data Summary for Tests in Circular Reactor Tube 26
2. Data Summary for Tests in Annular Reactor Tube 26 (a)
3. Material Balances for Tests in Circular Reactor Tube 27
4. Material Balances for Tests in Annular Reactor Tube 28
5. Product Yields for Tests With Rich Gas Feed 29
6. Calculated Equilibrium Temperatures for Tests in Circular Reactor Tube 33
7. Calculated Equilibrium Temperatures for Tests in Annular Reactor Tube 34

INTRODUCTION

Recent interest in acetylene and ethylene as raw materials for the chemical industry has stimulated a great deal of research on the thermal decomposition of low molecular weight hydrocarbons. However, despite the large amount of fundamental and applied work which has been carried out, there are still wide gaps in the data in the regions of industrial interest, particularly with regard to the optimum conditions for acetylene formation.

The key variables in the pyrolysis of light hydrocarbons are temperature, contact time, and partial pressure of the reactant. The objective of this project was to study the effect of these variables on the yields of ethylene and acetylene from pyrolysis of a stream of butane diluted by natural gas. Particular emphasis was placed on acetylene formation.

Butane was chosen as the hydrocarbon raw material because large quantities are expected to be available in Alberta with the commencement of large scale gas export. Available data and theoretical considerations indicated that high acetylene yields would be favored by carrying out the butane pyrolysis in the presence of a diluent gas. Natural gas was thought to have some advantages as a diluent, since after acetylene and ethylene recovery the remaining off gases could be used as fuel to supply most of the process heat. Also the resulting data should be helpful in assessing the possibilities of utilizing a rich natural gas

as feedstock for this type of process, thus eliminating the cost of butane separation and recovery. To investigate this latter proposal more fully a few tests were run feeding such a rich gas, containing significant amounts of ethane, propane, and butane directly to the pyrolysis furnace.

A continuous tubular ceramic reactor was used because of its relative simplicity, although the low heat transfer rates obtainable have prevented its industrial application for acetylene production.

THEORETICAL BACKGROUND

(a) Thermodynamics

All hydrocarbons are unstable at high temperatures and the final equilibrium pyrolysis products would be essentially carbon and hydrogen. Therefore, it is necessary to quench the reactions before equilibrium is reached. Rapid quenching is assisted by the endothermic nature of the pyrolysis reactions. Under the conditions used in this study appreciable amounts of methane, ethylene and acetylene were also present in the product gas.

Without making any assumptions as to the actual mechanism involved, these products may be considered as being formed by the following stoichiometric reactions.

Free energy changes and K_p values have been calculated over the range of temperature of interest in this investigation.

Table 1 FREE ENERGY CHANGES* (M BTU/lb.mol)

	1600°F	1800°F	2000°F	2200°F	2400°F
$C_4H_{10} = 4C + 5H_2$	-142.9	-163.1	-183.5	-203.9	-223.0
$C_4H_{10} = 2CH_4 + 2C + H_2$	-112.7	-122.3	-131.9	-142.3	-150.8
$C_4H_{10} = 2C_2H_4 + H_2$	-31.5	-44.1	-56.5	-69.1	-80.4
$C_4H_{10} = 2C_2H_2 + 3H_2$	-3.5	-28.7	-53.9	-79.1	-103.0

*Free energy data was obtained from Rossini (1)

Table 2 K_p VALUES

	1600°F	1800°F	2000°F	2200°F	2400°F
$C_4H_{10} = 4C + 5H_2$	34.9	36.3	37.5	38.6	39.2 (atm.^{4})
$C_4H_{10} = 2CH_4 + 2C + H_2$	27.5	27.3	27.0	26.9	26.5 (atm.^{2})
$C_4H_{10} = 2C_2H_4 + H_2$	7.5	9.8	11.6	13.1	14.2 (atm.^{2})
$C_4H_{10} = 2C_2H_2 + 3H_2$	0.9	6.4	11.0	15.0	18.2 (atm.^{4})

The following conclusions are evident:

1) The most favored reaction at all temperatures is that to carbon and hydrogen.

2) The equilibrium yields of ethylene, and particularly acetylene are increased by increasing temperature while the equilibrium yield of methane is relatively unaffected by temperature.

3) Since all reactions show a volume increase, they should be favored by a reduced partial pressure of butane in the feed.

A measure of the approach to equilibrium of the reactions forming the intermediate products methane, ethylene and acetylene may be obtained by considering the ethylene-acetylene and methane-acetylene equilibria. From the stoichiometric equation

$$C_2H_4 = C_2H_2 + H_2 \qquad K_p = (_pH_2)\frac{(_pC_2H_2)}{(_pC_2H_4)}$$

it may be shown that the C_2H_2/C_2H_4 ratio will be a function of the temperature and H_2 partial pressure only. Similarly it may be shown that the C_2H_2/CH_4 ratio is a function of temperature, H_2 partial pressure, and

CH_4 partial pressure.

$$2\ CH_4 = C_2H_2 + 3\ H_2 \qquad \frac{C_2H_2}{CH_4} = \frac{K_p(_pCH_4)}{(_p\ H_2)^3}$$

These equilibrium ratios have been calculated over a range of temperature and partial pressure. Details of the calculations are given in the appendix. The C_2H_2/C_2H_4 ratio is plotted as a function of temperature and H_2 partial pressure in Figure 1. The C_2H_2/CH_4 ratio is plotted as a function of temperature, H_2 partial pressure, and CH_4 partial pressure in Figure 2.

The heats of reaction calculated over a range of temperature are shown below.

Table 3 HEATS OF REACTION (M Btu/lb. mol)

	1600°F	1800°F	2000°F	2200°F	2400°F
$C_4H_{10} = 4C + 5\ H_2$	66.1	66.3	66.2	64.9	64.8
$C_4H_{10} = 2CH_4 + 2C + H_2$	-12.3	-12.5	-13.5	-14.1	-13.8
$C_4H_{10} = 2C_2H_4 + H_2$	98.3	98.1	97.6	96.7	96.0
$C_4H_{10} = 2C_2H_2 + 3\ H_2$	256.9	256.3	255.8	254.3	253.6

The formation of acetylene is seen to be strongly endothermic. The formation of ethylene and the decomposition to carbon and hydrogen are moderately endothermic, while the formation of methane is actually slightly exothermic. The heat of reaction does not vary significantly with temperature.

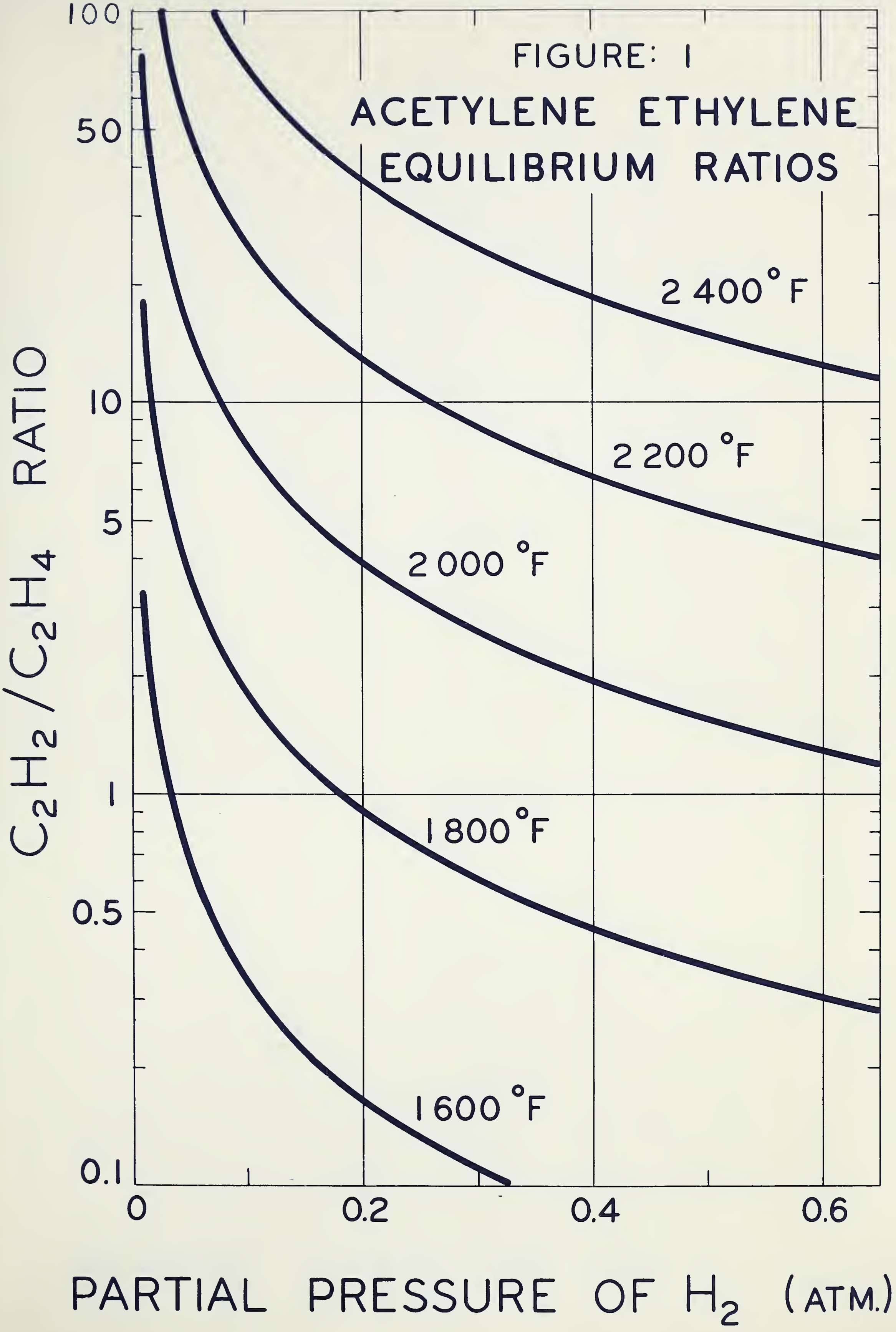


FIGURE: 1

ACETYLENE ETHYLENE EQUILIBRIUM RATIOS

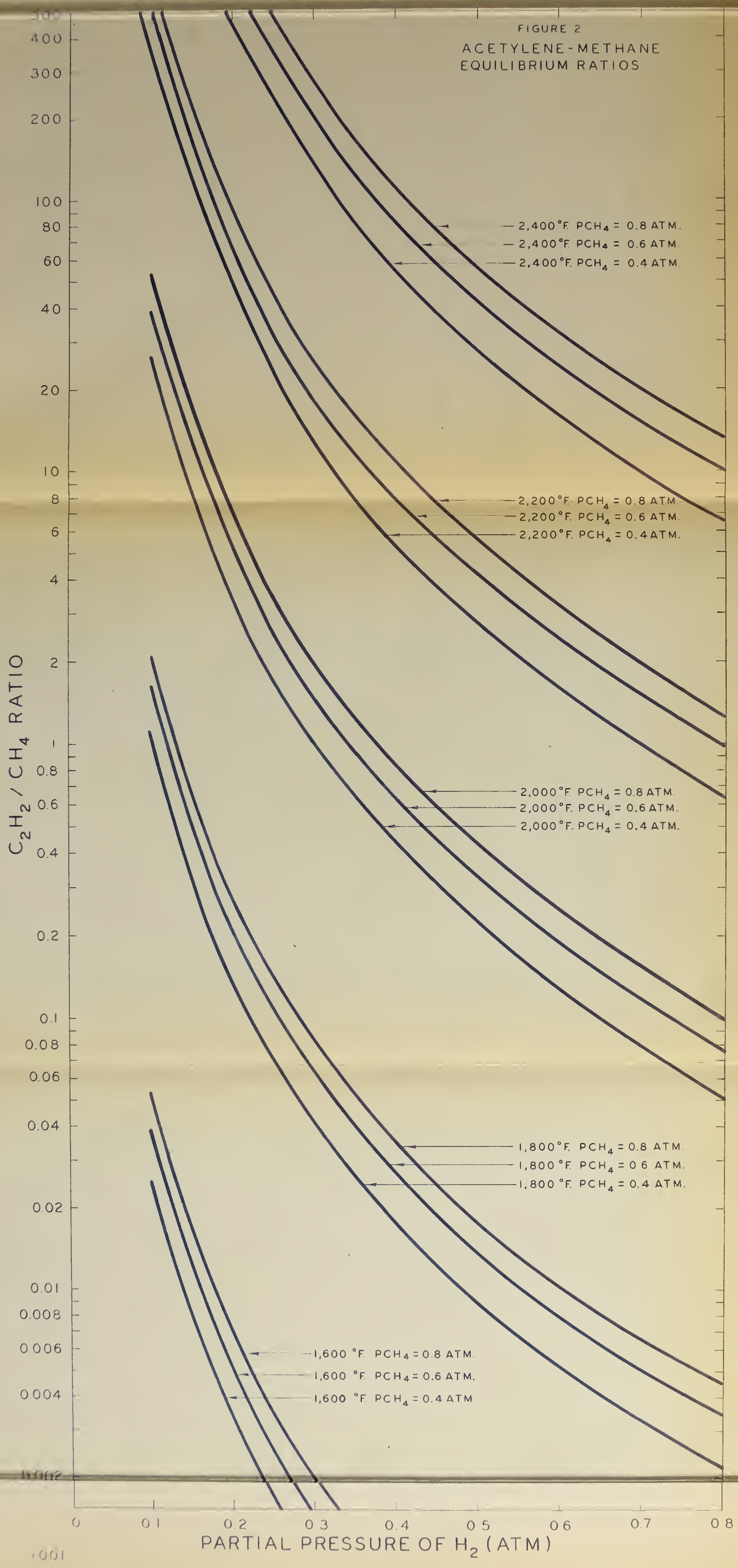


FIGURE 2

ACETYLENE-METHANE EQUILIBRIUM RATIOS

(b) Kinetics and Mechanism

The pyrolysis of the paraffin hydrocarbons to acetylene is considered to go through a series of intermediate reactions, with ethylene probably the most important product directly preceding acetylene formation (2).

The initial decomposition reactions of the paraffins are homogeneous and apparently follow a first order rate expression (2). However this simple relationship breaks down at high degrees of conversion and at both low and high pressures. Also the temperatures at which kinetic studies have been carried out are much lower than those obtained in this investigation.

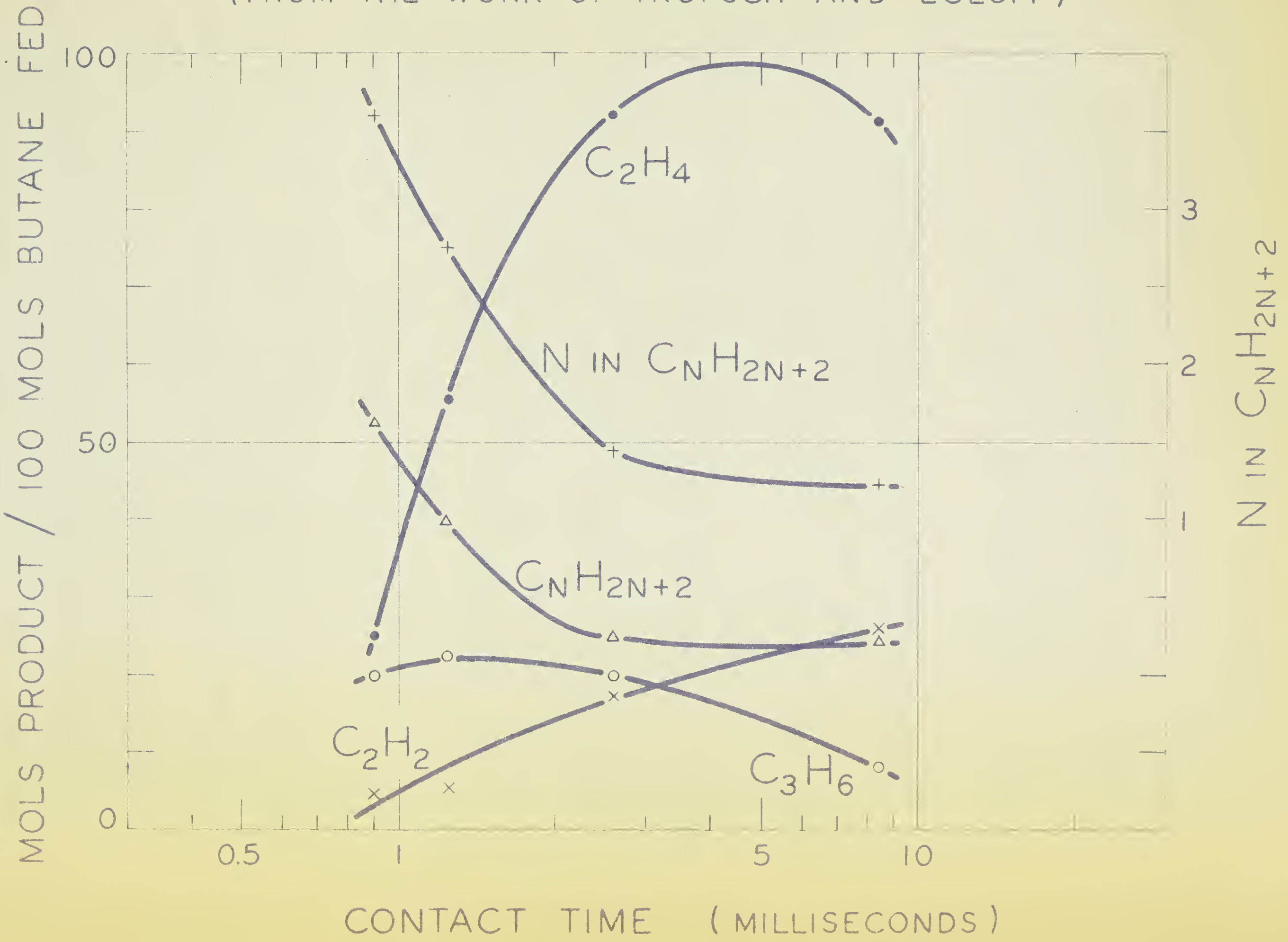
Data on the mechanism of hydrocarbon decomposition are rather sketchy and confined almost entirely to studies of methane and ethane pyrolysis. However it does appear that free radical mechanisms play an important part, at least in the initial decomposition reactions (2). There is evidence to indicate that the decomposition of ethylene to acetylene proceeds by a molecular mechanism. Once again the majority of the published data has been obtained at temperatures much lower than those encountered in this work.

Tropsch and Egloff pyrolyzed n-butane at 2000°F and 50 mm Hg. A graphical presentation of their data reproduced from Kramer and Happel (2) is shown in Figure 3. It is evident here that ethylene is the most important intermediate product preceding acetylene formation.

FIGURE: 3

PYROLYSIS OF NORMAL BUTANE
AT 2000° F AND 50 MM HG

(FROM THE WORK OF TROPSCH AND EGLOFF)



(c) Commercial Development

A good deal of effort has been devoted to the development of commercial processes for the production of acetylene by light hydrocarbon pyrolysis. At least three of these appear to have commercial possibilities.

a) The Schoch process, presently in the development stage at the University of Texas, uses a shaped electrical discharge to supply energy to the reacting gases. An effective pyrolysis temperature of 2600°F is reached and an off gas containing 10% acetylene is produced. However the high energy requirements of the acetylene producing reactions make the process uneconomical unless extremely cheap power is available.

b) The Sacchsse process is at present the only process in commercial use for acetylene manufacture by hydrocarbon pyrolysis. Energy is supplied by partial combustion of the reacting gases, and pyrolysis temperatures up to 2700°F are obtainable. Using pure oxygen for combustion an acetylene concentration of 8.5% in the off gas is obtained. To be economical the process requires utilization of the by product "synthesis gas", a mixture of carbon monoxide and hydrogen. Also the tonnage oxygen requirements make a large plant size necessary for economic operation.

c) The Wulff (Koppers-Hasche) (3) (4) process, with two pilot scale plants in operation, uses a regenerative type cracking furnace in which a refractory checkerwork alternately absorbs heat from fuel gas combustion and releases it to supply the necessary energy for

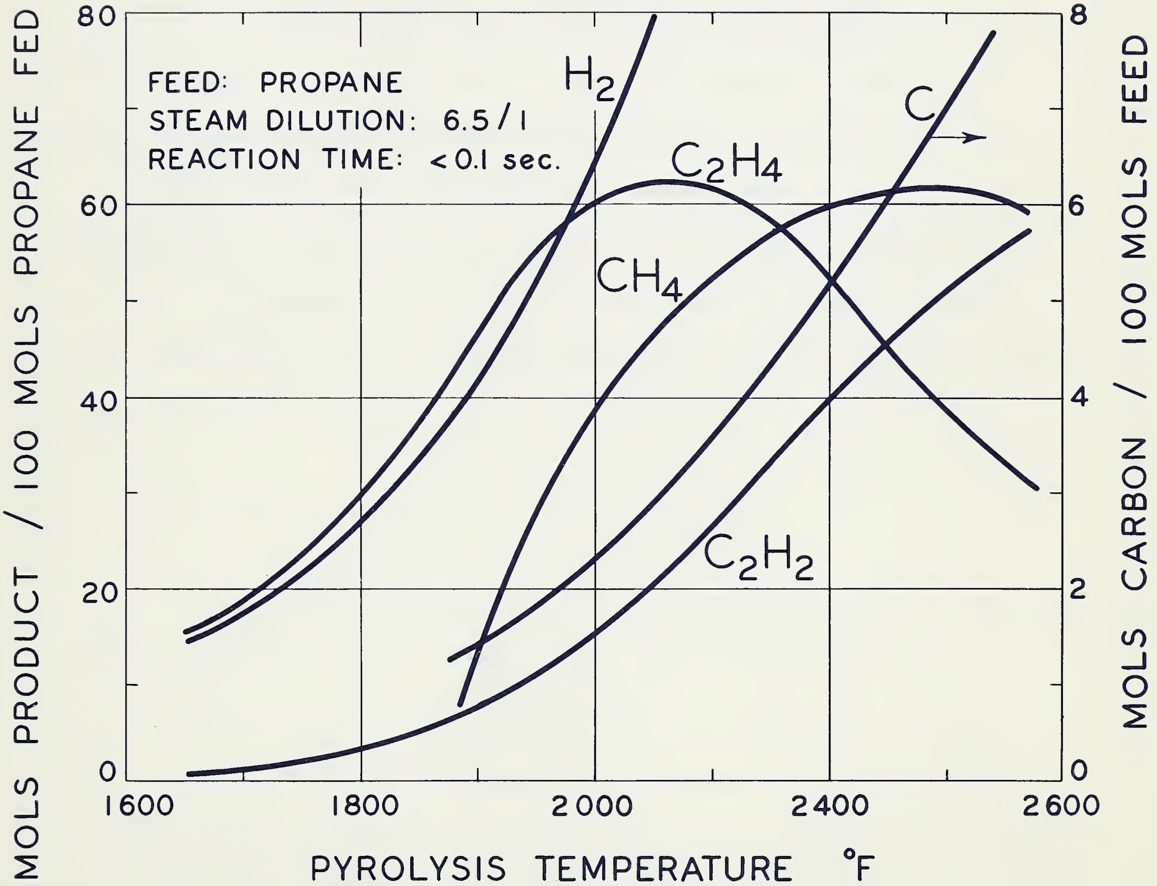
the pyrolysis reactions. Steam dilution is used to obtain a low hydrocarbon partial pressure during reaction and to reduce carbon black formation. Reaction temperatures of 2200 to 2400°F are reached. Acetylene yields are reported as 40-50 mols/100 mols of butane fed; ethylene yields are of similar magnitude. The usual disadvantages of non-continuous processes are present here - chiefly inefficient use of reactor volume and incomplete control of operating variables.

It is significant that all the above processes avoid the transfer of heat through a solid wall to the reacting gas. There are two reasons for this - the high energy requirements of the process and the high temperature level at which this energy must be supplied. The required high temperature can be withstood successfully only by ceramic materials. The low mechanical strength of the available materials necessitates a thick reactor wall, which in combination with their low thermal conductivity leads to an excessive temperature drop through the wall. In addition ceramic materials are difficult to fabricate into shapes having a high heat transfer area/reactor volume ratio.

A considerable amount of development work on the Wulff process was done by Hasche (5)(6)(7) using a tubular reactor, although it was eventually abandoned in favor of a regenerative type furnace. The feed was preheated to about 1800°F in a stainless steel coil in order to reduce the heat load in the ceramic tube. Hasche's data for the laboratory scale cracking of propane are presented in Figure 4. The same trends in product yields would be expected with a butane feed.

FIGURE: 4

PRODUCT DISTRIBUTION
FOR THE HASCHE PROCESS



Some data is available on the use of butane as a feed for the Wulff process and is of interest since reaction conditions are very similar to those of the present work. However much of this information is in the form of patent data and even in the published material reaction conditions are sketchily and incompletely described.

Some recent work by Linden (8) on the cracking of hydrocarbon feedstocks, including butane, also has a bearing on this investigation. A continuous reactor employing an electrically heated silicon carbide reactor tube was used. Operating temperatures of 2400 - 2500°F were obtained. Diluent steam was added to reduce the hydrocarbon partial pressure. Unfortunately the use of an inert diluent (steam) prevents direct comparison of any of this information with the results of the present work.

EQUIPMENT AND PROCEDURE

A flow diagram of the reaction system is shown in Figure 5. n-Butane was metered in the liquid state, vaporized and mixed with a metered stream of natural gas. This mixture was then passed through a silicon carbide reaction tube mounted vertically in a gas fired furnace. The cracked gas leaving the furnace was quenched in a water cooled section of pipe and passed through a glass cloth filter to remove the carbon formed during pyrolysis. A sample was taken at this point by means of a small diaphragm type pump. The gas was then cooled, metered and exhausted to vent.

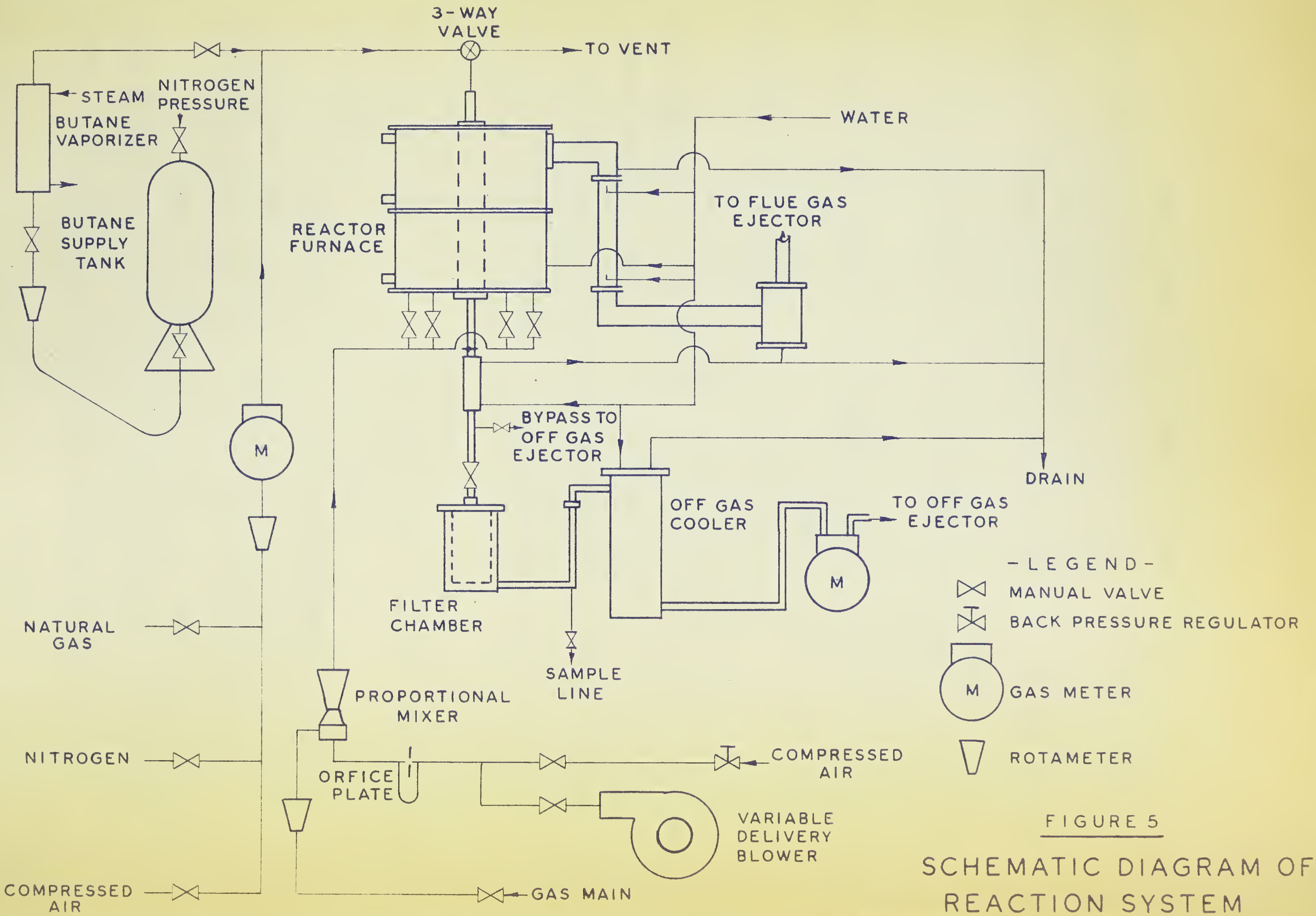


FIGURE 5

SCHEMATIC DIAGRAM OF REACTION SYSTEM

The furnace used is shown in Figures 6 and 7. It has been described in earlier work (9) so only a brief description will be included here. The overall dimensions were approximately four feet in diameter by four feet high. Between the fire chamber and the water cooled steel shell were a layer of fire brick, a layer of insulating brick and a layer of castable insulation. The fire chamber dimensions were twenty-four inches in diameter by thirty inches high at the centre. Premixed natural gas and air were supplied to four burners mounted in the floor of the furnace. Flue gases were water spray quenched and exhausted to vent. The furnace was operated at full thermal capacity during all tests.

Two different types of reaction tubes were employed. The first consisted of a 1-7/8 inch O.D. x 1-1/8 inch I.D. silicon carbide tube mounted as shown in Figure 8. The second consisted of a 2-3/4 inch O.D. by 2 inch I.D. silicon carbide tube with a 1-5/8 inch diameter corebuster. This assembly is shown in Figure 9. The tubes were mounted by bolting the base plate directly to the bottom of the furnace. The inlet to a tube was formed by cementing progressively smaller tubes inside the reactor tube until a 1 inch outside diameter was reached. A neoprene hose connected the reactor tube inlet to the feed gas system.

The cements used were either zirconia-cement fondu or alundum-cement fondu mixtures. With proper curing these exhibited very little shrinkage and stood up well at the temperatures encountered.

Pressures and differential pressures were measured by water filled manometers. Ejectors on the off gas and flue gas lines permitted control of pressures in both the reaction system and the fire chamber.

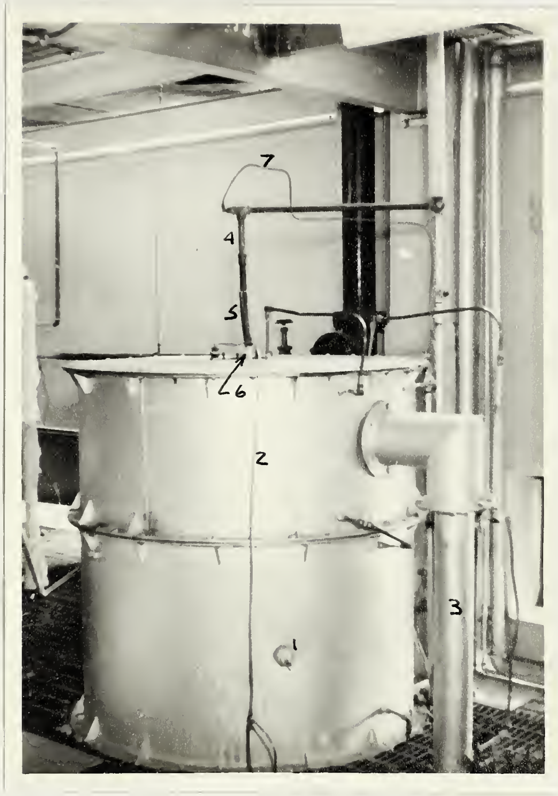


Figure 6

REACTOR FURNACE

1. Lighting Port
2. Furnace Pressure Tap
3. Water Spray Quench Tower for Flue Gases
4. Reactor Gas Inlet
5. Neoprene Tube
6. Reactor Tube Inlet
7. Reactor Tube Pressure Tap

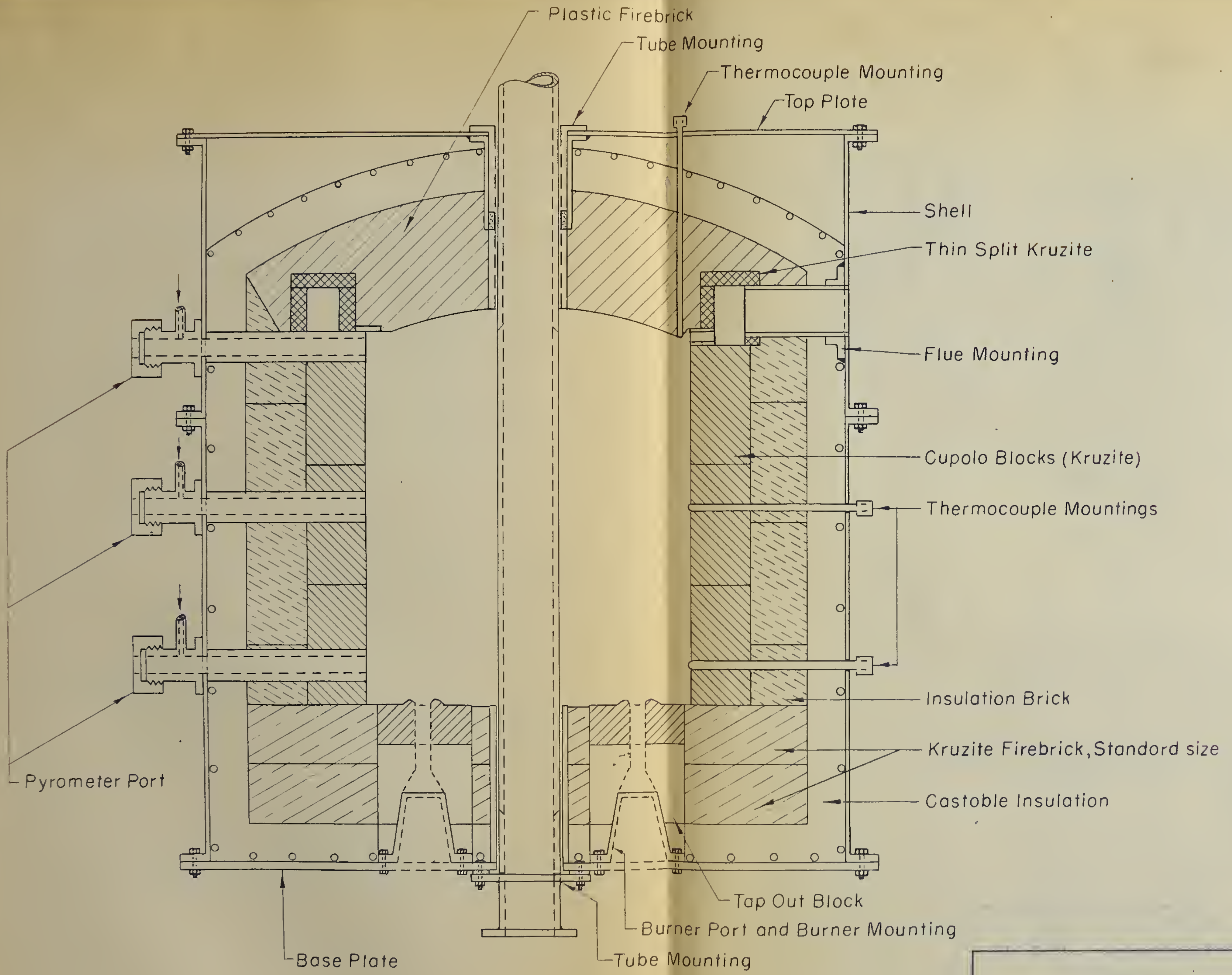


FIGURE 7

CARBON BLACK
FURNACE ASSEMBLY

Scale $1\frac{1}{2}$ Inch = 1 Feet

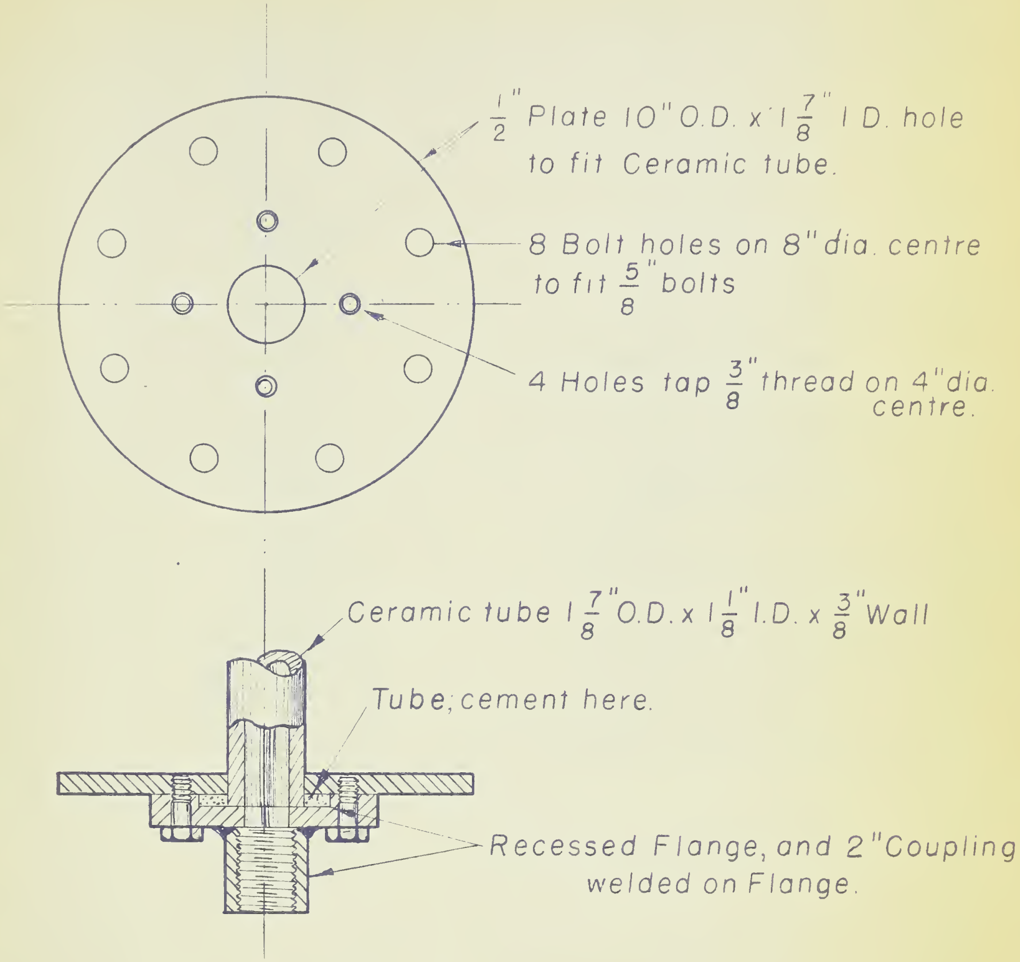

1/2" Plate 10" O.D. x 1 7/8" I.D. hole to fit Ceramic tube.
8 Bolt holes on 8" dia. centre to fit 5/8" bolts
4 Holes tap 3/8" thread on 4" dia. centre.
Ceramic tube 1 7/8" O.D. x 1 1/8" I.D. x 3/8" Wall
Tube; cement here.
Recessed Flange, and 2" Coupling welded on Flange.

FIGURE 8

MOUNTING PLATE AND FLANGE FOR PYROLYSIS TUBE

Pyrolysis of Normal Butane at High Temperature.

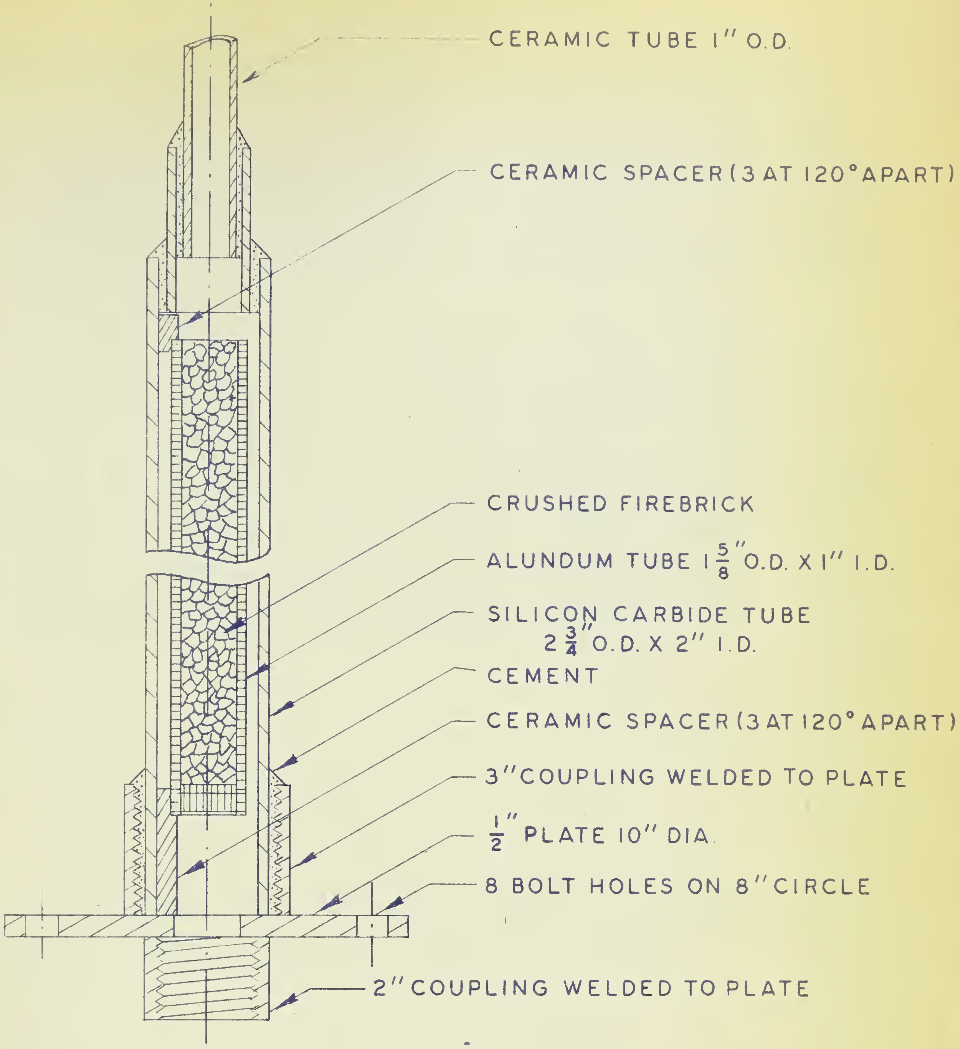

CERAMIC TUBE 1" O.D.
CERAMIC SPACER (3 AT 120° APART)
CRUSHED FIREBRICK
ALUNDUM TUBE $1\frac{5}{8}''$ O.D. X 1" I.D.
SILICON CARBIDE TUBE $2\frac{3}{4}''$ O.D. X 2" I.D.
CEMENT
CERAMIC SPACER (3 AT 120° APART)
3" COUPLING WELDED TO PLATE
$\frac{1}{2}''$ PLATE 10" DIA.
8 BOLT HOLES ON 8" CIRCLE
2" COUPLING WELDED TO PLATE

FIGURE 9

ANNULAR REACTOR TUBE

Butane flow was measured by a calibrated rotameter; gas flows were measured by bellows type domestic meters. Metering temperatures were measured by dial thermometers. Reaction tube temperatures were measured by a Leeds and Northrup optical pyrometer. The control panel arrangement is shown in Figure 10.

The product gases were analyzed by the Research Council of Alberta analytical staff using a Fisher-Gulf gas chromatography apparatus.

The butane used was commercial grade normal butane supplied by the Imperial Oil Limited Calgary Refinery. It analyzed 6.5% iso-butane. The diluent gas was Viking-Kinsella natural gas, obtained from the Northwest Utilities substation. This gas had the following analysis.

CH_2 = 91.0%
C_2H_6 = 2.0%
C_3H_8 = 0.5%
N_2 = 6.5%

All tests were of short duration due to plugging of the reactor tubes by carbon formed in the pyrolysis reactions.

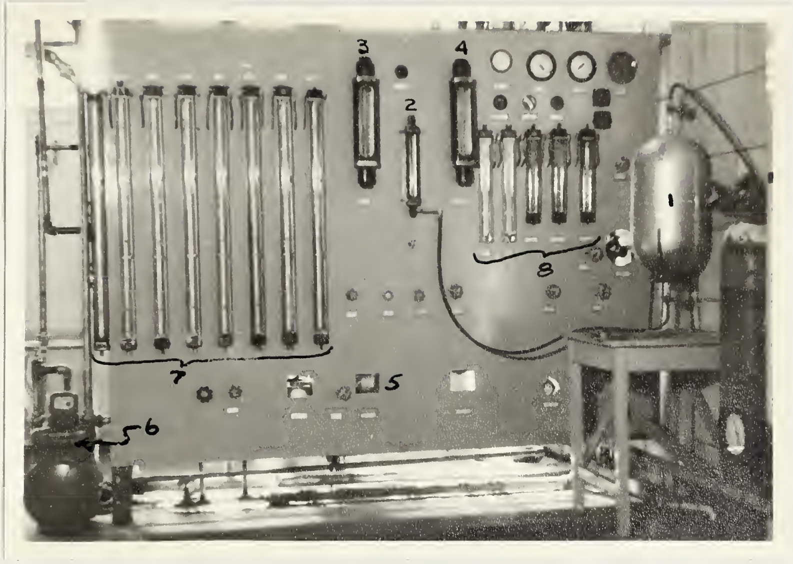


Figure 10

CONTROL PANEL

1. Butane Supply Tank
2. Butane Rotameter
3. Diluent Gas Rotameter
4. Fuel Gas Rotameter
5. Diluent Gas Meter
6. Off Gas Meter
7. Manometers to Various Points in the System
8. Service Control Rate Manometers

RESULTS

The pyrolysis of normal butane-natural gas mixtures was investigated at butane concentrations from 0 to 35% and at space velocities of 15, 25 and 35 seconds^{-1}. Space velocity is defined here as volumetric feed rate (measured at 2000°F and 700 mm)/reactor volume.

Outside wall temperatures of the reaction tube were measured using an optical pyrometer. For the circular reactor tube this temperature ranged from 2550 to 2650°F, depending on the heat load. For the annular reactor tube the temperature range was 2630 to 2700°F. Direct temperature measurements of the reacting gas were felt to be impractical for the following reasons:

1) Radiation effects, both from the tube walls and from reradiating carbon particles.

2) The possibility of a surface catalyzed reaction on the temperature measuring element.

The other major experimental difficulty was plugging of the reactor tubes with carbon formed during the pyrolysis reactions. This necessitated tests of short duration, especially at the more severe cracking conditions. Temperature measurements on the reactor tube during the course of a test indicated that, at least in the shorter tests, steady state operation was not reached. This fact is probably responsible for some of the scattering among the data, although sample collection was delayed until as late in the tests as possible.

The raw test data are tabulated in Table 1 for the 1-1/8 inch I.D. circular reactor tube and in Table 2 for the 2 inch x 1-5/8 inch annular reactor tube. Material balances for the tests with mixed natural gas-butane feeds are presented in Tables 3 and 4. Details of

the calculations are shown in the Appendix. These data have been plotted in Figures 11 to 16 which show mols of product formed/100 mols of feed as a function of the concentration of butane in the feed. Thus for a compound, such as methane, which is present in both the feed and product the figure plotted is the change in the number of mols during the reaction. Best fit curves were drawn by eye for CH_4, C_2H_4, and C_2H_2; the carbon and hydrogen yields were then adjusted to make the data internally self consistent. Data for further calculations were taken from these smoothed curves.

Another series of tests were made using a rich gas mixture of the following composition as feedstock.

CH_4 = 69.5%
C_2H_6 = 14.5%
C_3H_8 = 9.0%
C_4H_{10} = 2.5%
N_2 = 4.5%

Test data are included in Tables 1 and 2 and material balances are presented in Table 5. Product composition is shown graphically as a function of space velocity in Figure 17.

Yields of acetylene and ethylene were calculated as mols/100 mols of C_2 equivalent in the feed. These are plotted as a function of percent butane in the feed for the different space velocities in Figures 18 to 21.

Ethylene and acetylene yields from the rich gas feed were

FIGURE: 11

PRODUCT DISTRIBUTION PYROLYSIS OF NORMAL BUTANE WITH NATURAL GAS DILUTION.

$1\frac{1}{8}$" I.D. REACTION TUBE; SPACE VELOCITY = 15 $sec.^{-1}$

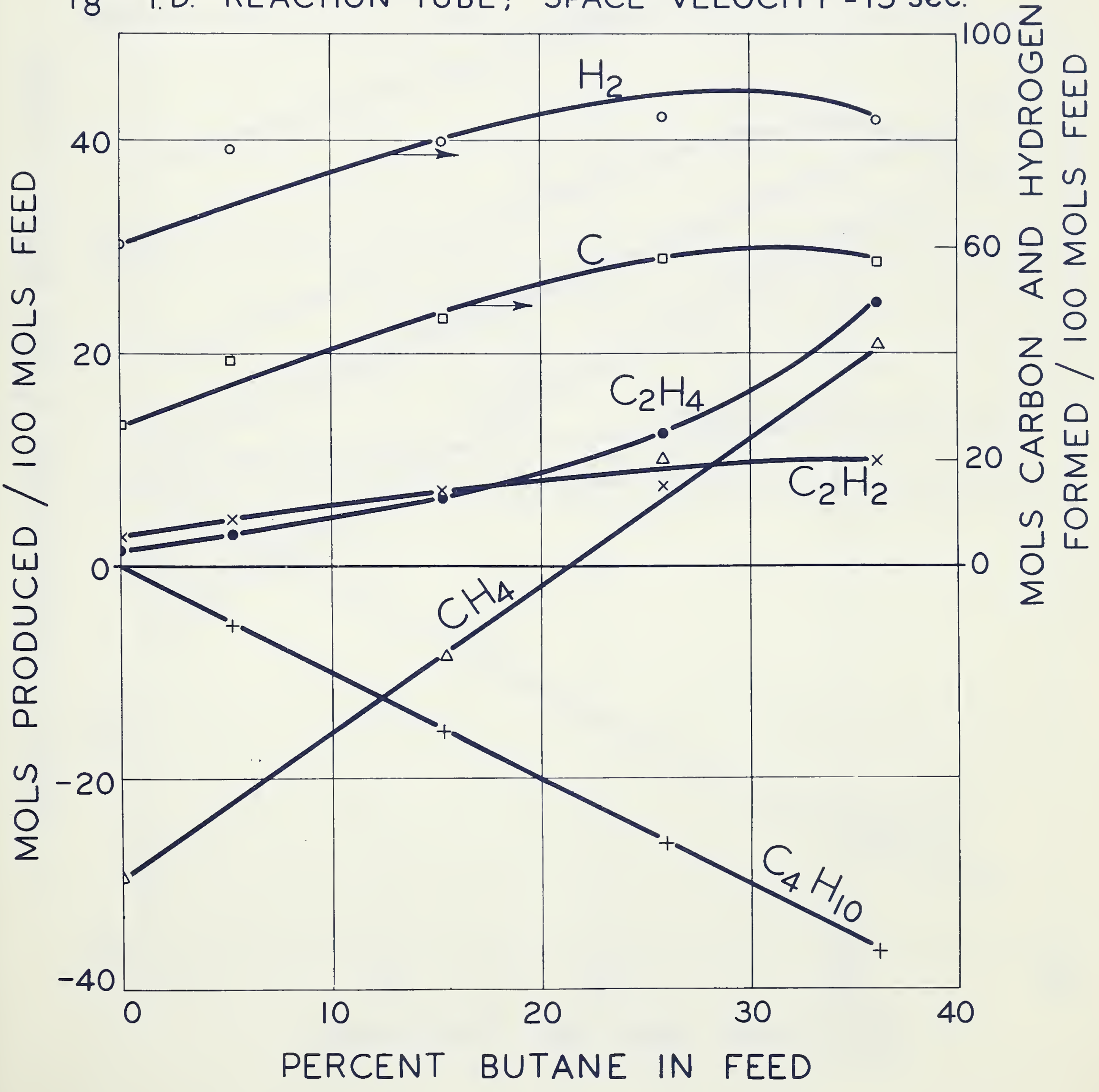


FIGURE: 12

PRODUCT DISTRIBUTION PYROLYSIS OF NORMAL BUTANE WITH NATURAL GAS DILUTION.

$1\frac{1}{8}''$ I.D. REACTION TUBE; SPACE VELOCITY = 25 $sec.^{-1}$

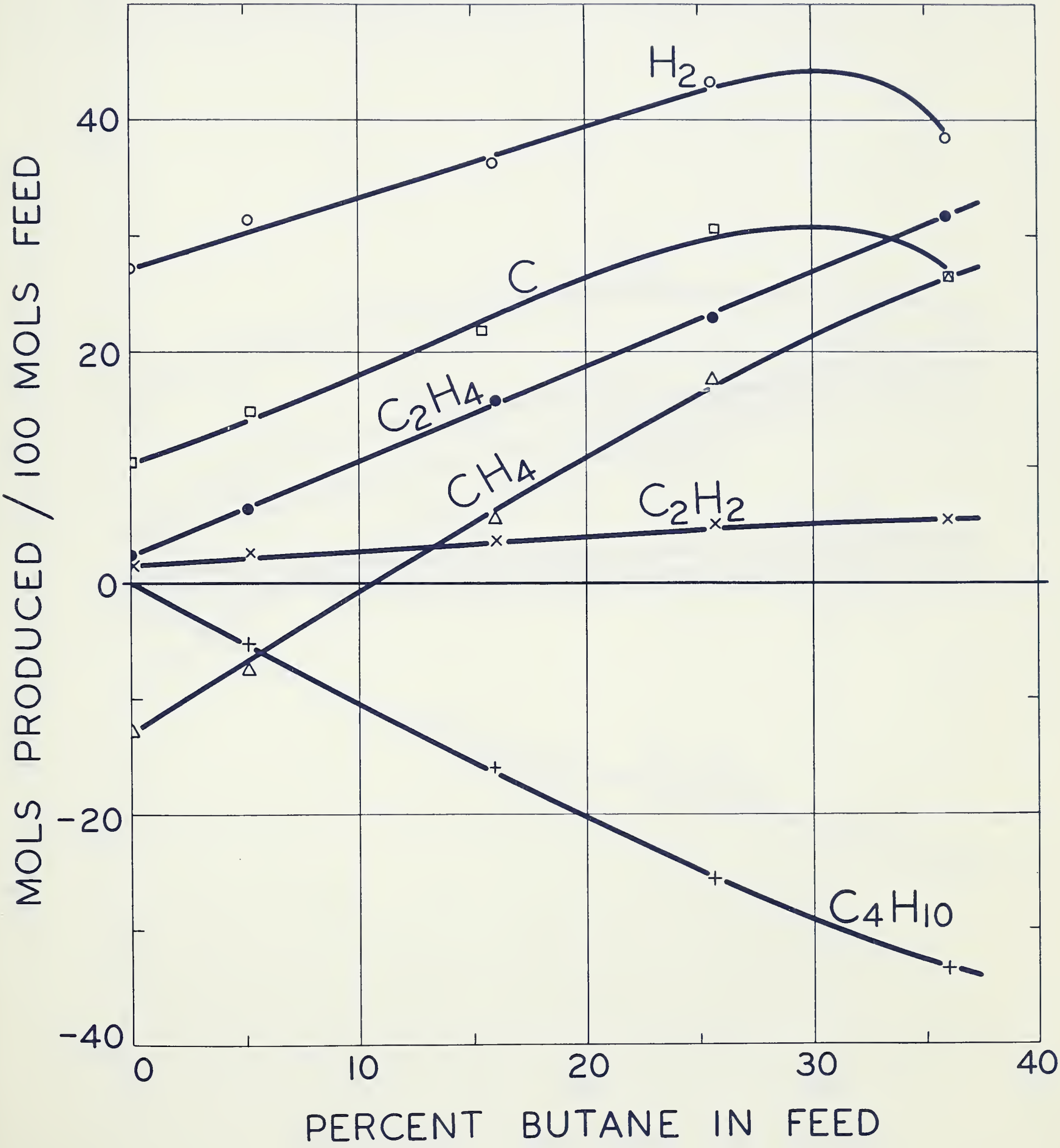


FIGURE: 13

PRODUCT DISTRIBUTION PYROLYSIS OF NORMAL BUTANE WITH NATURAL GAS DILUTION.

$1\frac{1}{8}''$ I.D. REACTION TUBE; SPACE VELOCITY = 35 sec.$^{-1}$

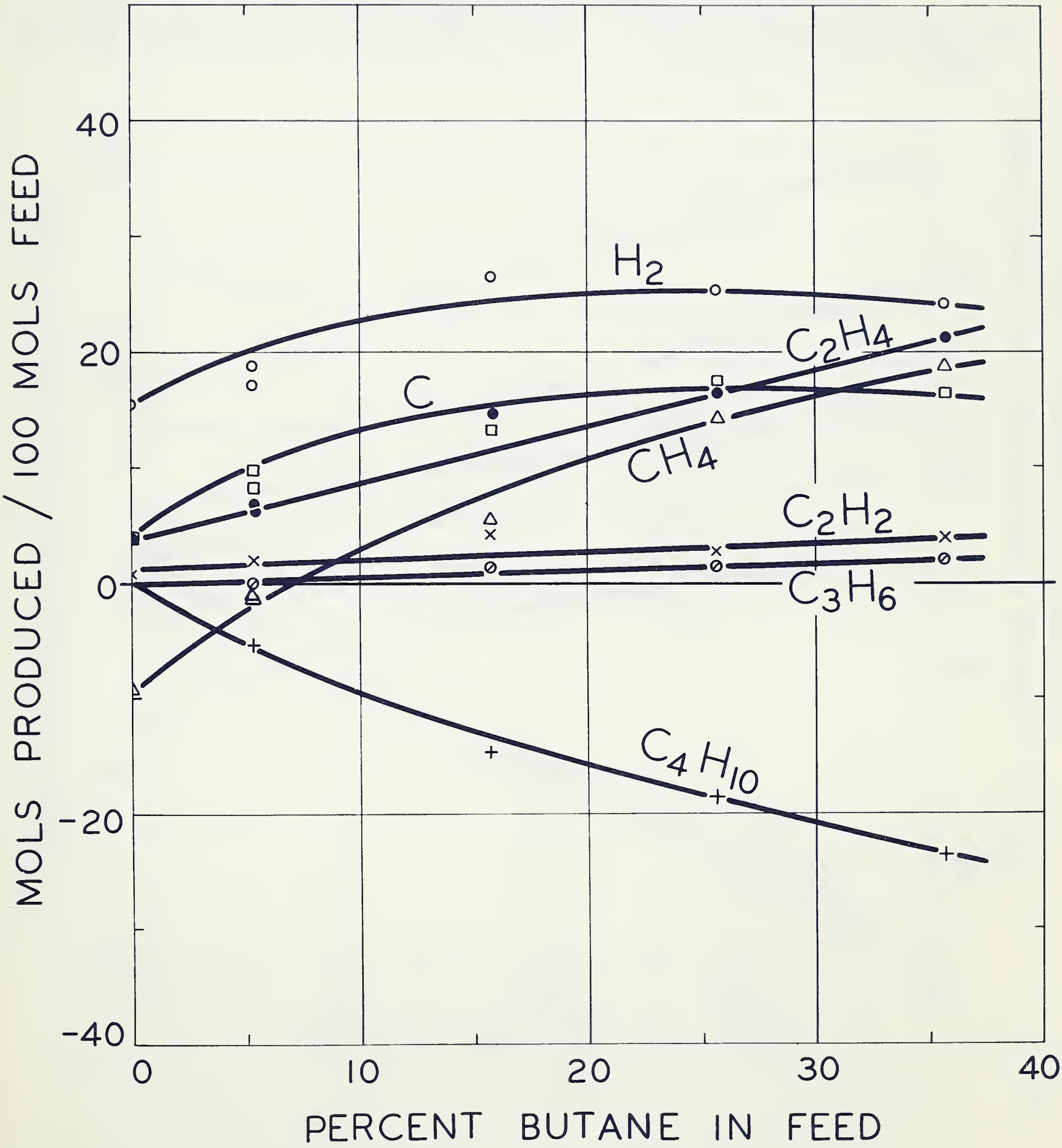
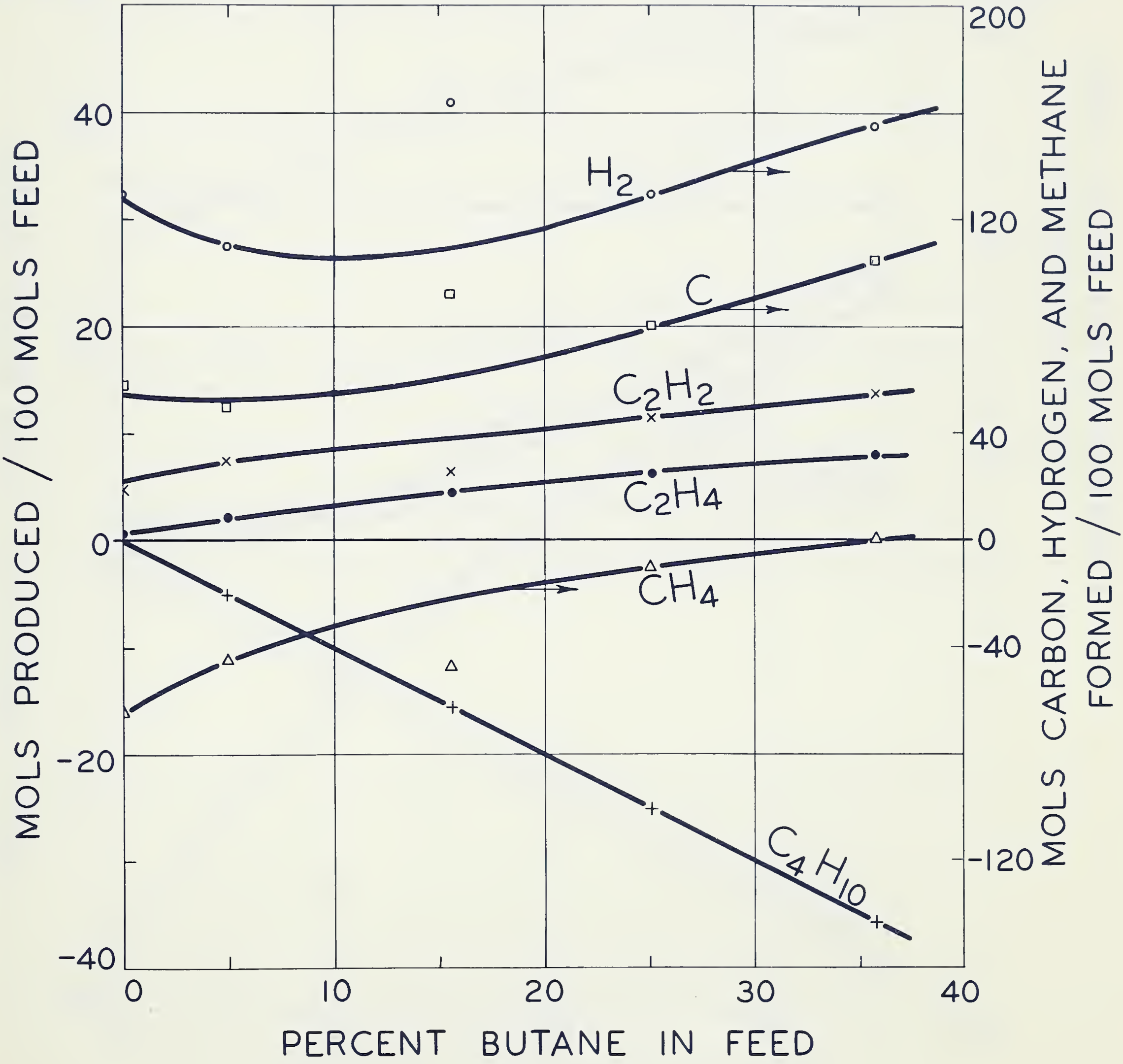


FIGURE: 14

PRODUCT DISTRIBUTION PYROLYSIS OF NORMAL BUTANE WITH NATURAL GAS DILUTION.

2" × 1 5/8" ANNULAR REACTION TUBE; SPACE VELOCITY = 15 sec.$^{-1}$



[illegible]

[illegible]

FIGURE: 15

PRODUCT DISTRIBUTION PYROLYSIS OF NORMAL BUTANE WITH NATURAL GAS DILUTION.

2"x1$\frac{5}{8}$" ANNULAR REACTION TUBE; SPACE VELOCITY = 25 sec.$^{-1}$

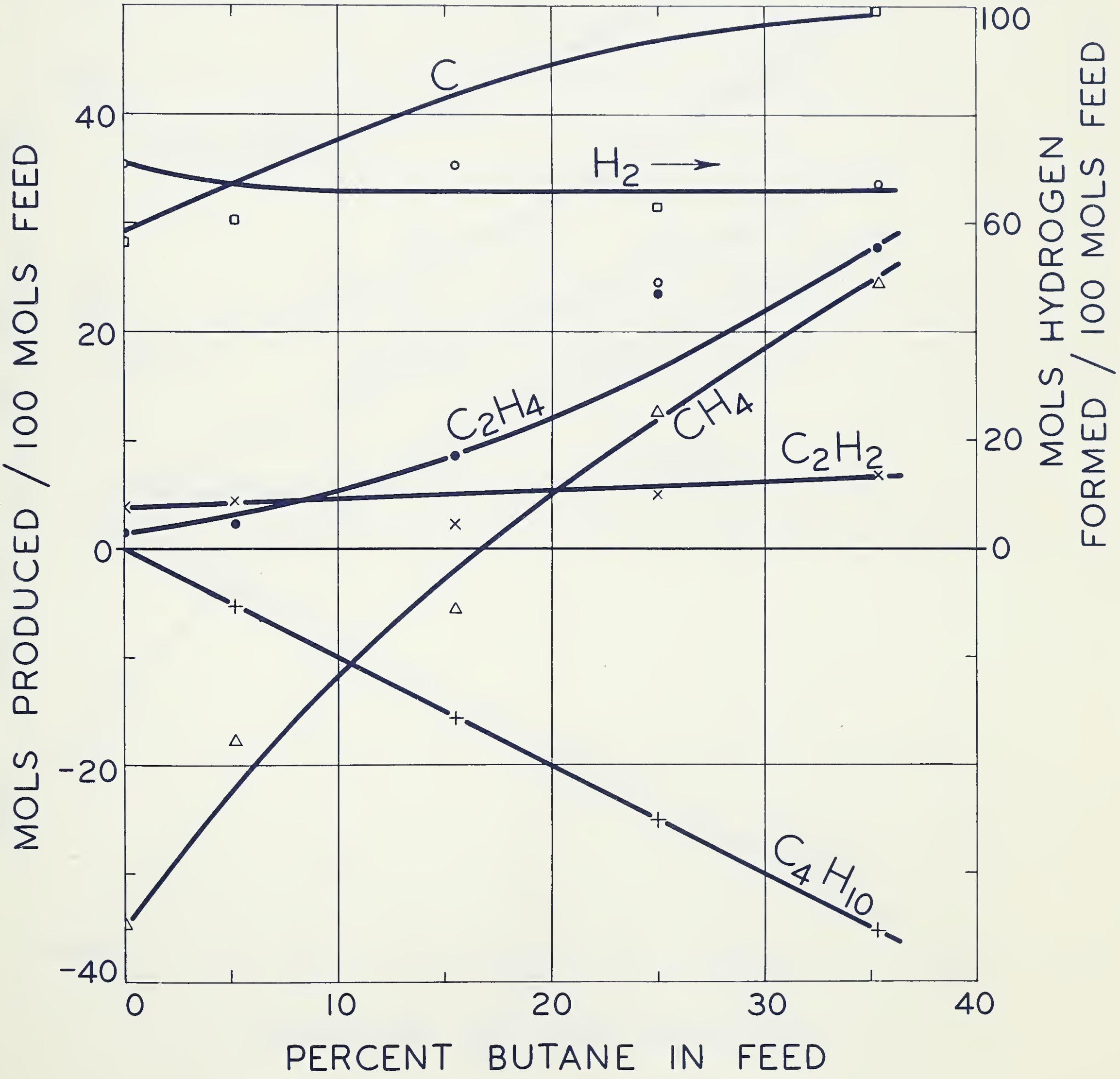


FIGURE: 16

PRODUCT DISTRIBUTION PYROLYSIS OF NORMAL BUTANE WITH NATURAL GAS DILUTION.

2"x$1\frac{5}{8}$" ANNULAR REACTION TUBE; SPACE VELOCITY = 35 sec.$^{-1}$

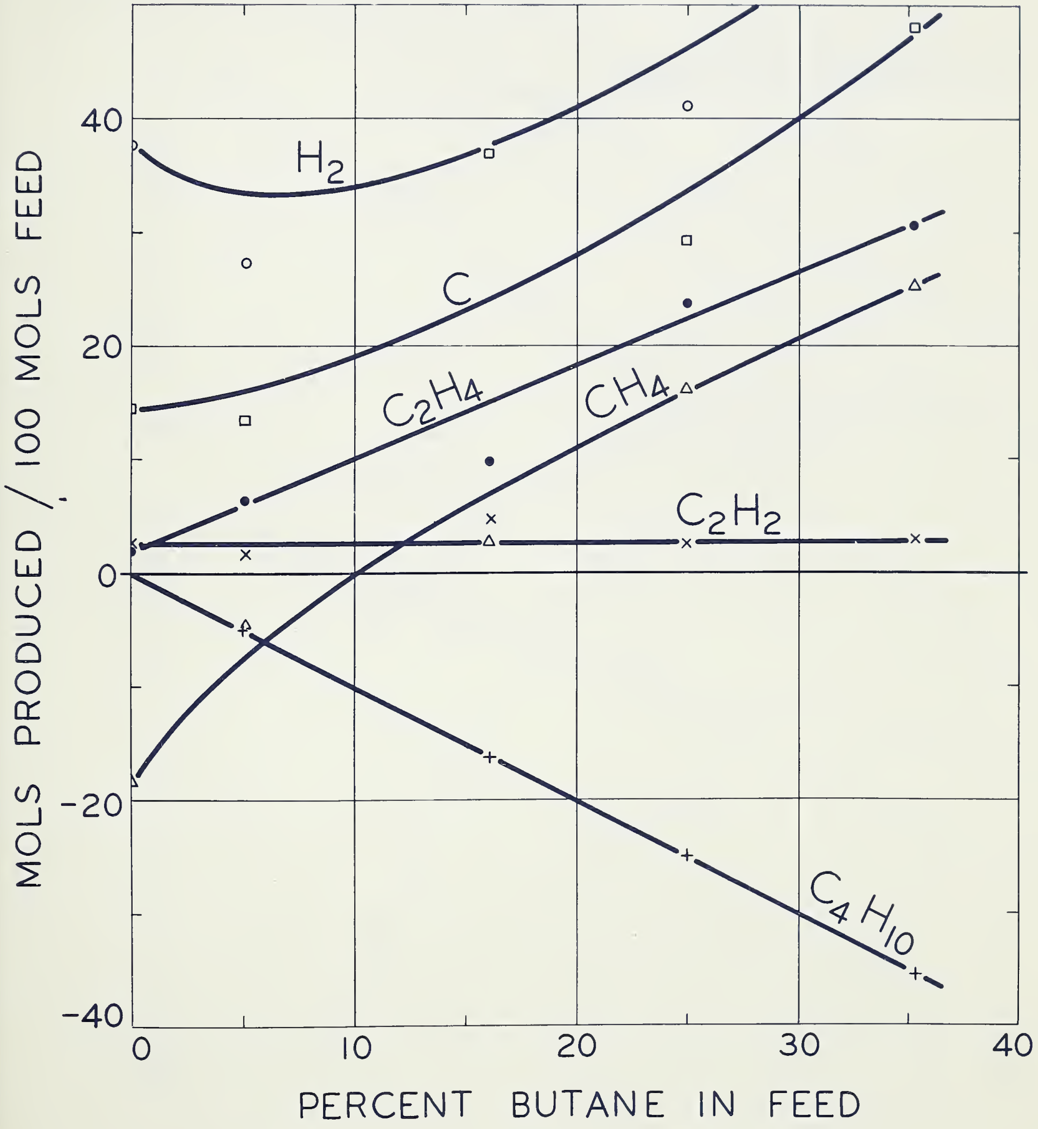
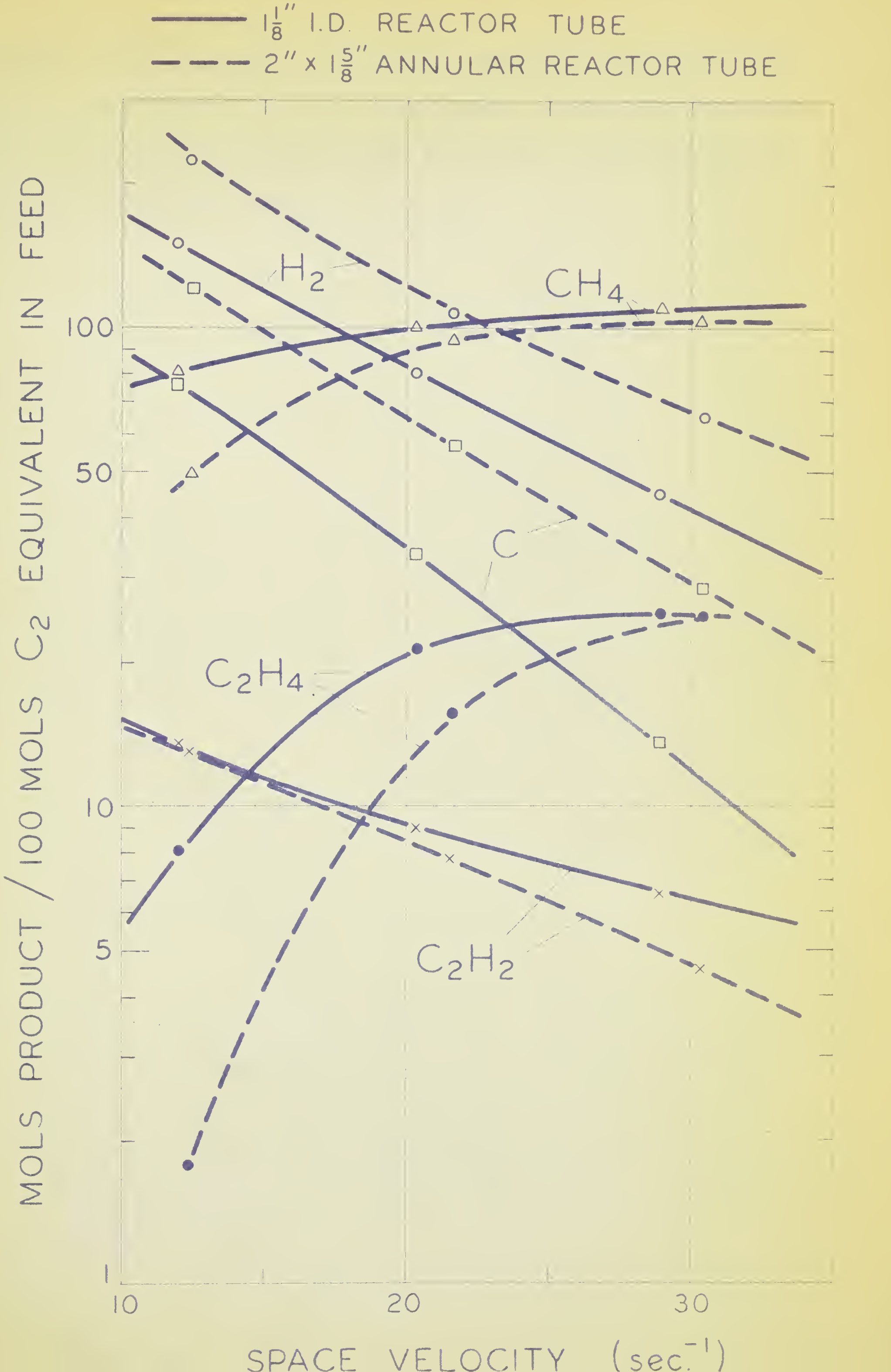


FIGURE 17

PYROLYSIS OF RICH NATURAL GAS



compared to the yields from a 13 percent butane plus lean natural gas feed with approximately the same carbon number. Results are shown in Figures 22 to 25, which also indicate the effect of space velocity on ethylene and acetylene yields.

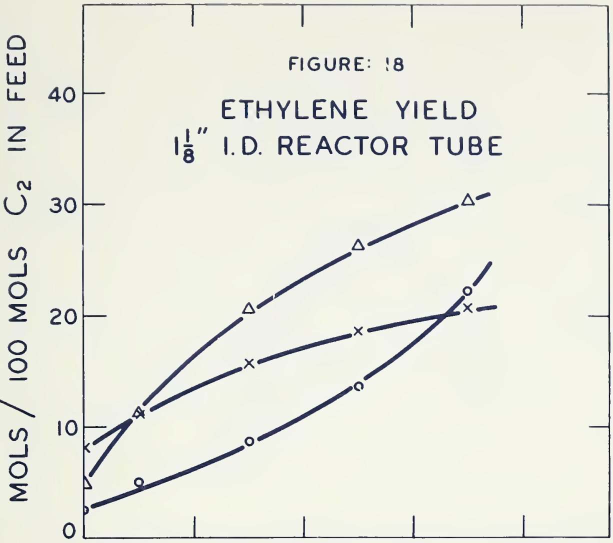


FIGURE: 18

ETHYLENE YIELD $1\frac{1}{8}''$ I.D. REACTOR TUBE

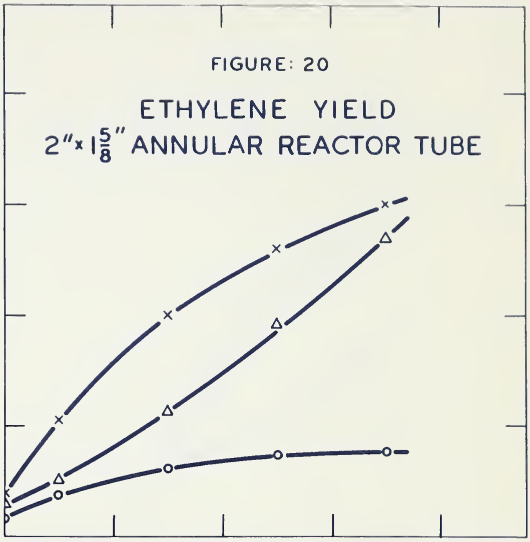


FIGURE: 20

ETHYLENE YIELD $2'' \times 1\frac{5}{8}''$ ANNULAR REACTOR TUBE

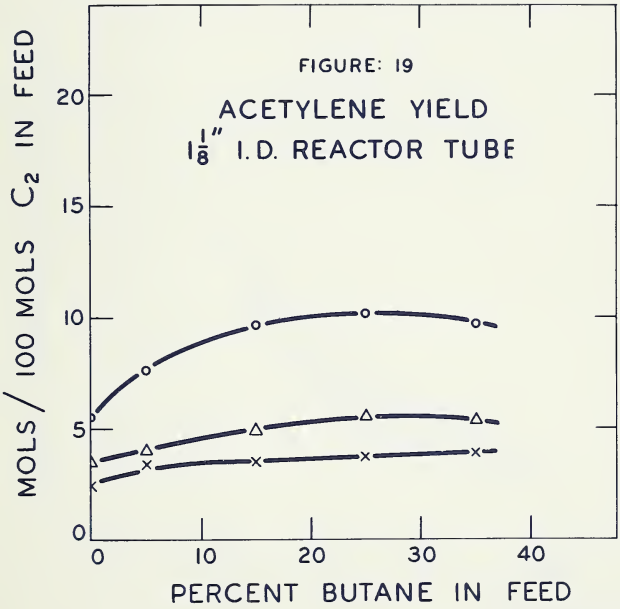


FIGURE: 19

ACETYLENE YIELD $1\frac{1}{8}''$ I.D. REACTOR TUBE

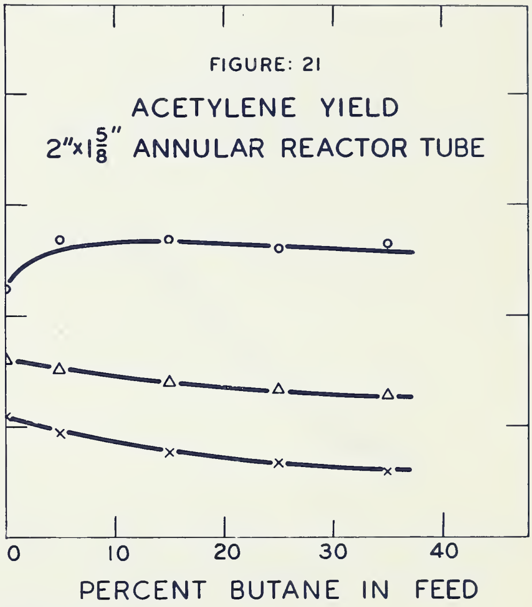


FIGURE: 21

ACETYLENE YIELD $2'' \times 1\frac{5}{8}''$ ANNULAR REACTOR TUBE

LEGEND

○ 15 $sec.^{-1}$

△ 25 $sec.^{-1}$

× 35 $sec.^{-1}$

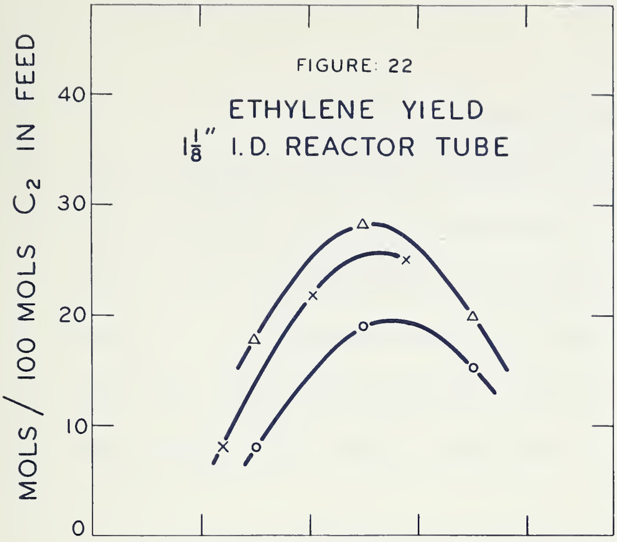


FIGURE: 22

ETHYLENE YIELD
$1\frac{1}{8}''$ I.D. REACTOR TUBE

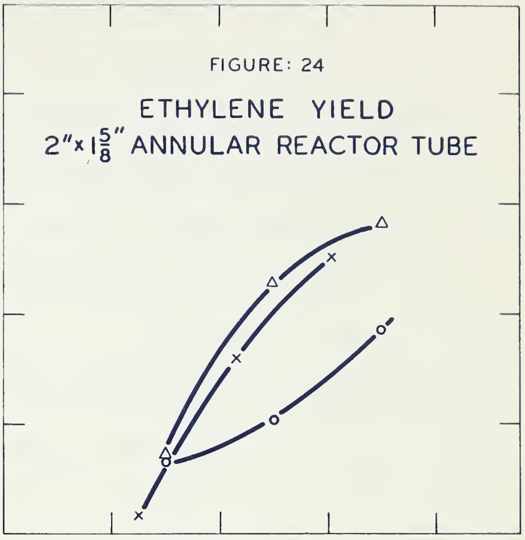


FIGURE: 24

ETHYLENE YIELD
$2'' \times 1\frac{5}{8}''$ ANNULAR REACTOR TUBE

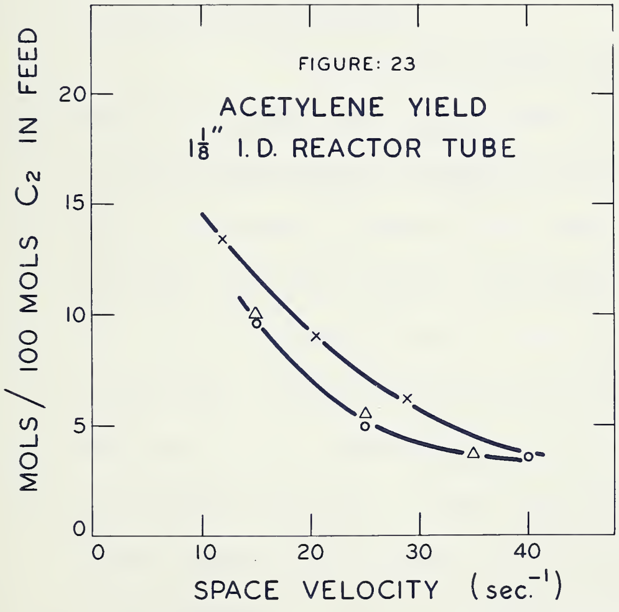


FIGURE: 23

ACETYLENE YIELD
$1\frac{1}{8}''$ I.D. REACTOR TUBE

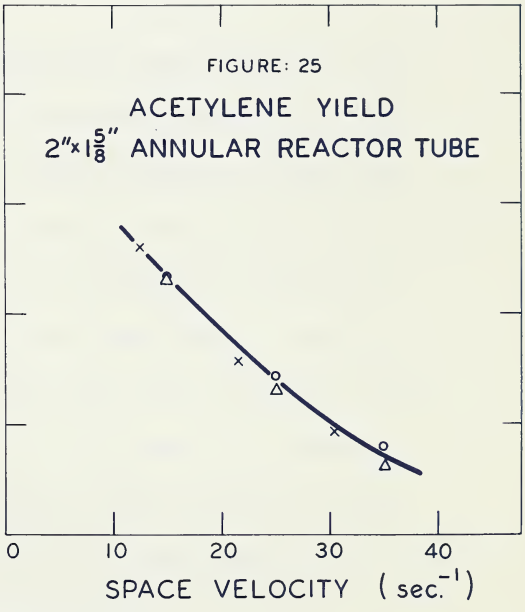


FIGURE: 25

ACETYLENE YIELD
$2'' \times 1\frac{5}{8}''$ ANNULAR REACTOR TUBE

LEGEND
- × RICH GAS FEED
- o 13 % BUTANE FEED
- △ 30% BUTANE FEED

DISCUSSION AND CONCLUSIONS

Evaluation of the separate effects of temperature, percent butane and space velocity on the acetylene and ethylene yields is difficult since in this reactor the temperature is a function of the heat load, which in turn is dependent on the other two variables. As no direct temperature measurements were available, an effort was made to estimate upper and lower gas temperature limits at various reaction conditions from heat transfer and chemical equilibria considerations.

Gas Temperature Estimation

For each test the gas temperatures corresponding to the measured C_2H_2/C_2H_4 and C_2H_2/CH_4 ratios were obtained from Figures 1 and 2. These temperatures, listed in Tables 6 and 7, provide a lower limit for the temperature reached by the reacting gases. Maximum gas temperatures calculated from heat transfer considerations are shown as a function of heat load in Figures 26 and 27. The postulated heat transfer mechanism assumed heat transfer by convection from the tube walls to the gas and by radiation from the tube walls to a cloud of carbon particles formed in the pyrolysis reactions. These carbon particles were assumed to be in thermal equilibrium with the gas. Details of these calculations are shown in the Appendix.

For purposes of comparison several of the calculated equilibrium temperatures were included in Figures 26 and 27. At high heat loads (i.e. low reaction temperatures) the temperature estimates from equilibrium considerations approach the temperature arrived at from heat

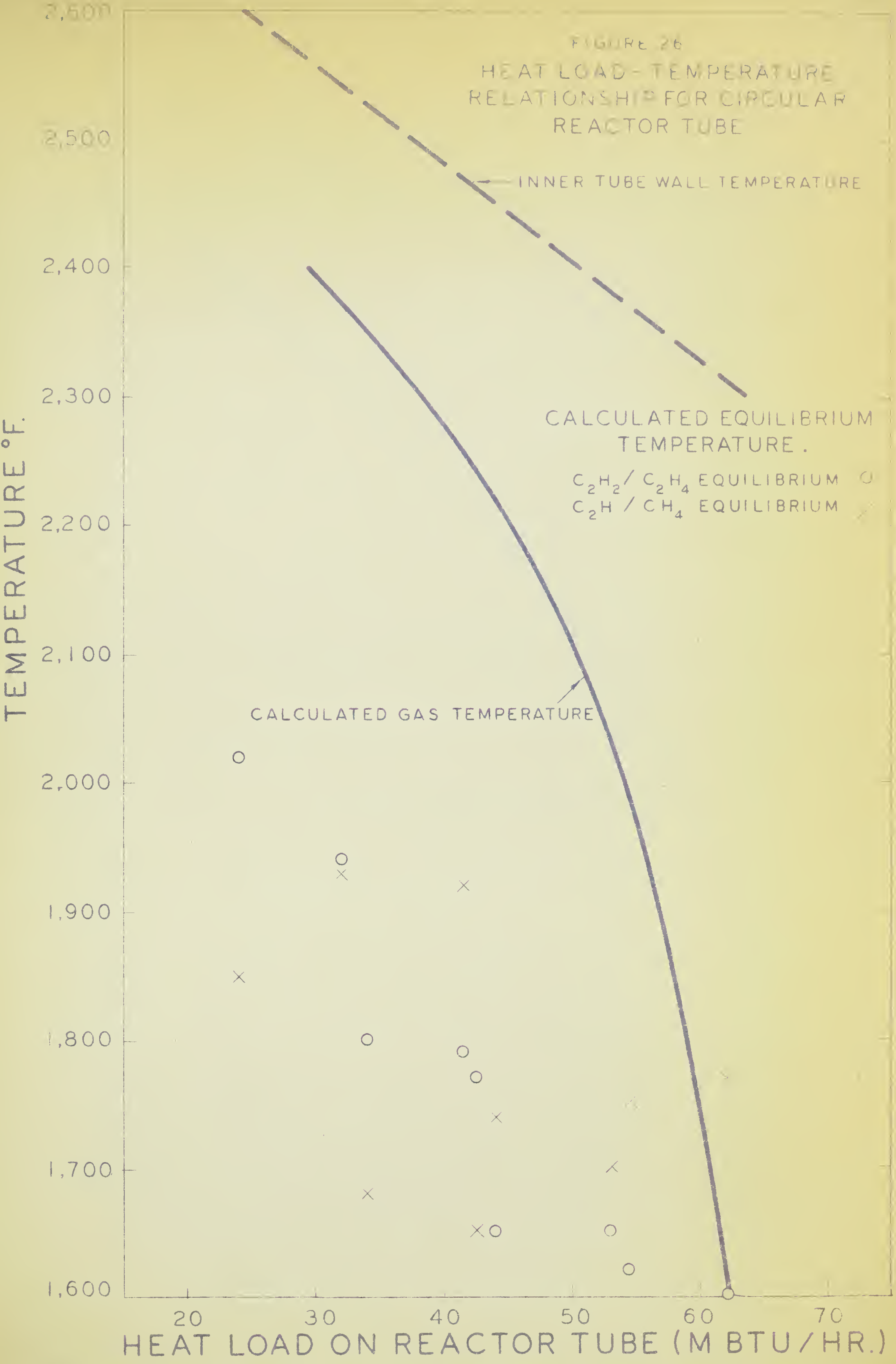


FIGURE 26
HEAT LOAD - TEMPERATURE RELATIONSHIP FOR CIRCULAR REACTOR TUBE

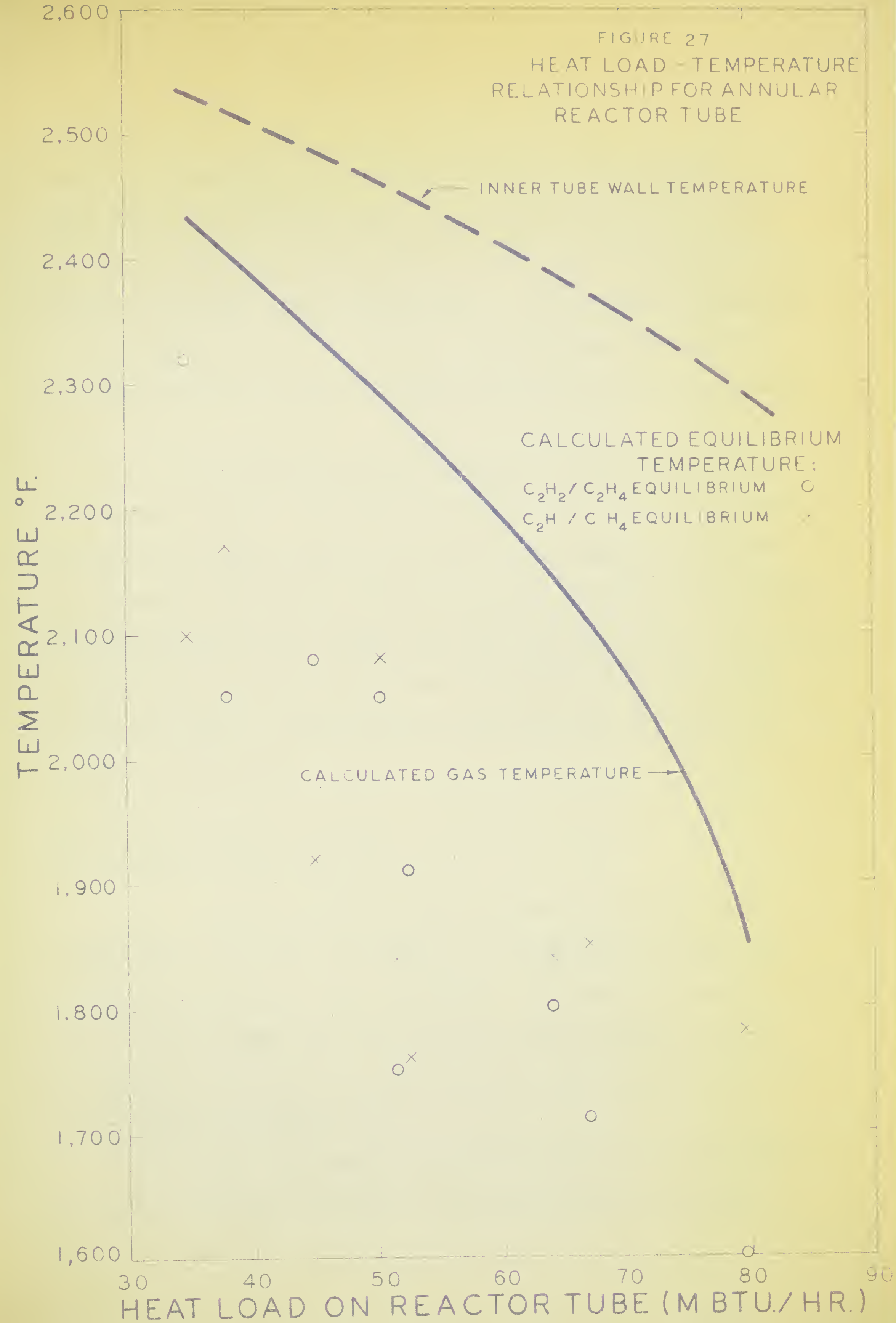


FIGURE 27
HEAT LOAD - TEMPERATURE RELATIONSHIP FOR ANNULAR REACTOR TUBE

transfer considerations, but at low heat loads (i.e. high reaction temperatures) the equilibrium temperature estimates are much below the expected gas temperature. This result indicates that equilibrium was not reached at the higher reaction temperatures. The most tenable explanation for this is that the equipment could not supply the required energy for the highly endothermic acetylene forming reactions at the high temperature levels.

This conclusion was confirmed by a consideration of the reaction heats involved. The energy requirements for pyrolysis of a 15% butane feed at a space velocity of 25 sec^{-1} and a temperature of 2400°F were calculated. Equilibrium yields of CH_4, C_2H_4, and C_2H_2 and very little free carbon formation were assumed. The resulting heat load was 105 M Btu/hr. However at this temperature the maximum calculated heat transfer rates are only 30 M Btu/hr. for the circular reactor tube and 40 M Btu/hr for the annular reactor tube.

Effect of Percent Butane in Feed

(a) The ethylene yield is increased by increasing the percent butane in the feed. This result is attributed to a higher rate of decomposition for butane than for methane. The higher rate would be expected since a comparison of the activation energies shows a value of 59 k cal/mol for the initial butane decomposition (10) compared to 79 kcal/mol for methane decomposition (2).

(b) The acetylene yield shows an initial increase with percent butane in the feed, which can be explained by the same reasoning as

in (a). However the increase in yield is not nearly as marked and with further increases in percent butane the yields level off and then begin to decline. Two factors are probably contributing here

(1) The lower temperatures accompanying an increase in the percent butane in the feed lower the equilibrium concentration of acetylene.

(2) Once appreciable quantities of butane are present in the feed the rate controlling reaction is probably the decomposition of ethylene to acetylene. The activation energy of this reaction has been estimated as 77 kcal/mol (2) and hence the reaction may be slightly faster than the methane decomposition but is probably much slower than the butane decomposition.

(c) The rich gas feed gave more ethylene and about the same amount of acetylene as a 13% butane-methane mixture with the same carbon number except for the acetylene yields in the circular reactor tube which are inconsistent with the rest of the data. The increased ethylene yield can be explained by examining the analysis of the two feeds:

Rich Gas Feed	Butane-Natural Gas Feed
CH_4 = 69.5%	CH_4 = 79.5%
C_2H_6 = 14.5%	C_2H_6 = 1.7%
C_3H_8 = 9.0%	C_3H_8 = 0.4%
C_4H_{10} = 2.5%	C_4H_{10} = 13.0%

Since the rich gas feed contains less methane and more of the more reactive hydrocarbons, the rate of ethylene formation would be higher than for the butane-natural gas feed.

Effect of Space Velocity

The effect of space velocity is complementary to the effect of temperature since raising the temperature and lowering the space velocity both increase the severity of the pyrolysis conditions. In the reactor used in this study any increase in space velocity was accompanied by a decrease of temperature due to the increased heat load; hence it is difficult to say whether the effects observed are primarily the result of space velocity or temperature changes.

Over the range of space velocities studied the ethylene yields increased with increased space velocity and in several instances passed through a maximum. This was expected, since the ethylene yield will certainly pass through a maximum with respect to reaction time.

The acetylene yield fell off with increasing space velocity which indicates that the maximum acetylene yield would be reached at a space velocity below those employed in this investigation. The rate of acetylene formation will certainly be governed by the rate at which energy can be supplied to the reactants, hence the higher acetylene yields at the lower space velocities would be expected.

Heat Transfer Limitations

The two reactor tubes employed in this investigation are described in the equipment section. The annular tube had the better heat transfer characteristics as a comparison of the heat transfer surface/

reactor volume ratios will show

Annular tube - surface/volume ratio = 71 ft^2/ft^3

Circular tube - surface/volume ratio = 43 ft^2/ft^3

A higher heat input/unit time and higher temperature were therefore obtained in the tests in the annular tube. A comparison of the energy absorbed and maximum temperature reached by the reacting gases is given below.

TABLE 4

EFFECT OF REACTOR TUBE GEOMETRY ON HEAT TRANSFER

	Circular Tube			Annular Tube		
Space Velocity	15	25	35	15	25	35
% Butane in Feed	13	35	35	13	35	35
Calculated Gas[1] Temperature (°F)	2370	1850	1610	2395	2110	1860
Heat Absorbed[2] by Reactants (MBtu/hr)	31.8	54.5	62.2	40.5	66.9	79.5

1. Gas temperature was calculated from heat transfer considerations
2. Assuming the product gases left the furnace at the calculated gas temperature.

Examination of the experimental data showed the following effects resulting from the higher heat input to the annular reactor tube:

(1) Indicated equilibrium temperatures were generally higher in the annular reactor tube.

(2) The ethylene maximum was reached at a higher space velocity (i.e. shorter contact time) in the annular reactor tube.

(3) Acetylene yields were higher at all space velocities in the annular reactor tube.

(4) Much more carbon and hydrogen were formed in the annular reactor tube.

The major limitation on the practicability of a highly endothermic process such as this is the rate at which energy can be supplied to the reacting system. As previously indicated the high heat fluxes and high temperature drops necessary make heat transfer through a wall impractical. For example at the highest head load encountered in this investigation the heat flux was approximately 70 M Btu/ft^2 and the total temperature drop from the furnace to the reacting gases in the order of 1000°F. By comparison in the regenerative furnace described by Farnsworth (4) the heat transfer rates are in the order of 10,000 Btu/ft^2 with a temperature drop of 150°F.

In conclusion then it may be said that the pyrolysis of a natural gas stream rich in ethane, propane and butane appears to be a practicable commercial source of ethylene and acetylene in Alberta, if a suitable means of supplying the high energy requirements of the process at a high temperature level can be devised.

In order to gain some idea of the possibilities of meeting the energy requirements of the process by using the off gas from acetylene and ethylene recovery as fuel an energy balance was worked out for the following hypothetical conditions.

Feed - 15% butane + lean natural gas

Reaction temperature - 2400°F

Products - Equilibrium amounts of CH_4, C_2H_4, C_2H_2, and H_2.

Negligible free carbon formation.

Results on the basis of 100 lb. mols of feed entering at 75°F and the pyrolysis products leaving at 2400°F were:

Pyrolysis energy requirements = 13,760 M Btu

Energy available from off gas combustion assuming no sensible heat recovery = 12000 M Btu.

Energy available from off gas combustion assuming 50% of the flue gas sensible heat is recovered, say by preheating combustion air, = 17,450 M Btu.

It therefore appears that the process off gases could supply most or all of the energy requirements of the process.

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APPENDIX

MATERIAL BALANCE CALCULATIONS

EXAMPLE - Run No. 23

Feed Composition		Product Composition (Adjusted for N_2 Balance)	
CH_4	= 67.6%	CH_4	= 52.2%
C_2H_6	= 1.5	C_2H_6	= 1.0
C_3H_8	= 0.4	C_2H_4	= 14.1
C_4H_{10}	= 25.7	C_2H_2	= 3.1
N_2	= 4.8	H_2	= 26.6
	100.0	N_2	= 3.0
			100.0

Feed Gas Rate = 4.63 std. cfm (32°F and 1 atm.)

H_2 Balance

Feed - 269.8 mols H_2/100 mols feed gas

Product - 165.3 mols H_2/100 mols product gas

$\therefore$ Volumes product/volume feed = 269.8/165.3 = 1.63

Check:

Calculated off gas rate = (1.63)(4.63) = 7.55 cfm

Measured off gas rate = 7.3 cfm

Carbon Balance

Carbon in feed = 174.6 mols/100 mols feed

Carbon in off gas = $\underline{144.2}$ mols/100 mols feed

Carbon black formed = 30.4 mols/100 mols feed

OVERALL BALANCE - BASIS 100 MOLS FEED

	Feed	Product	Change in Reaction
CH_4	67.6	85.0	+17.4
C_2H_6	1.5	1.6	+0.1
C_2H_4	-	23.0	+23.0
C_2H_2	-	5.0	+5.0
C_3H_8	0.4	-	-0.4
C_4H_{10}	25.7	-	-25.7
H_2	-	43.3	+43.3
N_2	4.8	4.8	-
C	-	30.4	+30.4

SPACE VELOCITY CALCULATION

EXAMPLE - Run. No. 23

$$\text{Space Velocity} = \frac{\text{Feed Rate } (\text{ft}^3/\text{sec})}{\text{Reactor Volume } (\text{ft}^3)}$$

All space velocities were calculated at 700 mm and 2000°F.

Feed rate = 4.63 std cfm (32°F and 760 mm)

$$= \frac{4.63}{60} \times \frac{2460}{492} \times \frac{760}{700} \ \text{ft}^3/\text{sec.}$$

Reactor Volume:

Dimensions of Reaction Zone = 1-1/8" diam x 30" long

$$\text{Volume} = \left(\frac{9}{8}\right) \frac{\pi}{4} \left(\frac{1}{144}\right) (2.5) = 0.01726 \ \text{ft}^3$$

$$\text{Space Velocity} = \frac{4.63}{60} \times \frac{2460}{492} \times \frac{760}{700} \times \frac{1}{0.01726} = 24.3 \ \text{sec}^{-1}$$

TABLE 1 - DATA SUMMARY - TESTS IN CIRCULAR REACTOR TUBE

RUN NO.	2	3	4	7	8	9	10	11	12	13	14	15	16	17	18	20	21	22	23	24	25
Space Velocity (Sec.$^{-1}$)	11.9	25.5	33.7	14.2	33.4	23.6	34.3	24.3	14.6	14.1	34.3	24.1	14.5	28.9	20.3	33.1	33.4	33.9	24.3	14.5	12.0
Run Time (Min)	2.4	6.5	3.8	4.2	8.2	6.6	8.1	8.7	7.7	5.1	8.8	8.3	3.3	8.5	5.9	6.3		7.7	8.1	6.7	4.8
Feed Composition (Mol %)																					
CH_4	91.0	91.0	91.0	91.0	86.1	76.4	67.7	58.3	77.0	86.1	58.5	86.2	67.4	69.5	69.5	91.0	76.7	86.1	67.6	58.1	69.5
C_2H_6	2.0	2.0	2.0	2.0	1.9	1.7	1.5	1.3	1.7	1.9	1.3	1.9	1.5	14.5	14.5	2.0	1.7	1.9	1.5	1.3	14.5
C_3H_8	0.5	0.5	0.5	0.5	0.5	0.4	0.4	0.3	0.4	0.5	0.3	.5	0.4	9.0	9.0	0.5	0.4	0.5	0.4	0.3	9.0
C_4H_{10}	-	-	-	-	5.3	16.0	25.6	36.0	15.4	5.3	35.7	5.2	25.9	2.5	2.5	-	15.7	5.3	25.7	36.1	2.5
N_2	6.5	6.5	6.5	6.5	6.2	5.5	4.8	4.2	5.5	6.2	4.2	6.2	4.8	4.5	4.5	6.5	5.5	6.2	4.8	4.2	4.5
Expansion (Volume Cracked Gas) (Volume Feed Gas)	1.51	1.16	1.14	1.33	1.18	1.44	1.40	1.71	1.62	1.51	1.48	1.26	1.78	1.36	1.50		1.37	1.19	1.63	2.16	1.75
Product Composition(Mol %)																					
CH_4	26.0	67.4	70.6	46.5	71.9	57.0	58.0	49.5	41.0	38.9	52.1	62.6	41.2	55.0	46.6	74.6	60.2	71.2	52.2	39.0	31.3
C_2H_6	1.0	0.1	0.1	-	1.0	0.5	1.0	1.0	0.2		2.0	0.5	0.1	3.3	0.5	0.8	0.8	1.0	1.0	0.2	-
C_2H_4	1.0	2.0	2.0	1.0	5.7	10.9	11.7	18.4	3.8	2.0	14.3	5.0	6.6	12.6	9.8	3.6	10.7	5.2	14.1	12.2	3.1
C_2H_2	3.1	1.5	1.5	2.0	1.6	2.5	2.0	3.1	4.2	3.0	2.6	2.0	4.1	3.3	4.1	0.7	3.1	1.5	3.1	4.9	5.2
C_3H_6	-	-	-	-	-	-	1.0	1.5	-	-	1.5	-	-	-	-	-	1.0	-	-	-	-
C_4H_{10}	-	-	-	-	-	-	5.1	1.5	-	-	8.2	-	-	-	-	-	0.7	-	-	-	-
H_2	64.7	23.5	20.1	45.4	14.5	25.3	17.9	22.5	47.5	52.2	16.3	25.2	45.1	22.5	36.2	14.3	19.5	15.9	26.6	41.5	57.9
N_2	4.2	5.5	5.7	5.1	5.3	3.8	3.3	2.5	3.3	3.9	3.0	4.7	2.6	3.3	2.8	6.0	4.0	5.2	3.0	2.2	2.5
Carbon Black Formed (Mols/Mol Feed)	0.418	0.103	0.080	0.266	0.080	0.218	0.177	0.265	0.467	0.390	0.164	0.148	0.580	0.092	0.227	0.037	0.133	.097	0.304	0.574	0.516

TABLE 2 - DATA SUMMARY - TESTS IN ANNULAR REACTOR TUBE

RUN NO.	27	28	29	30	31	32	34	35	36	37	38	39	40	41	42	43	44	45
Space Velocity (Sec.$^{-1}$)	30.4	21.6	12.5	34.9	15.3	24.7	34.6	24.3	14.4	32.5	24.7	14.6	24.6	35.0	15.0	14.6	34.5	25.0
Run Time (Min)	2.9	2.7	0.9	2.3	1.5	1.7	3.0	2.7	1.5	1.7	2.7	1.2	2.2	3.3	1.5	1.9	4.5	3.5
Feed Composition (Mol %)																		
CH_4	69.5	69.5	69.5	91.0	91.0	91.0	58.9	76.9	76.8	76.3	58.8	58.4	86.2	68.2	68.1	86.4	86.3	68.2
C_2H_6	14.5	14.5	14.5	2.0	2.0	2.0	1.3	1.7	1.7	1.7	1.3	1.3	1.9	1.5	1.5	1.9	1.9	1.5
C_3H_8	9.0	9.0	9.0	0.5	0.5	0.5	0.3	0.4	0.4	0.4	0.3	0.3	0.5	0.4	0.4	0.5	0.5	0.4
C_4H_{10}	2.5	2.5	2.5	-	-	-	35.3	15.4	15.6	16.1	35.4	35.8	5.2	25.0	25.1	5.0	5.1	25.0
N_2	4.5	4.5	4.5	6.5	6.5	6.5	4.2	5.5	5.5	5.5	4.2	4.2	6.2	4.9	4.9	6.2	6.2	4.9
Expansion (Volume Cracked Gas) (Volume Feed Gas)	1.42	1.59	2.01	1.22	1.68	1.39	1.84	1.57	2.09	1.59	1.91	1.98	1.43	1.59	2.09	1.68	1.24	1.65
Product Composition (Mol %)																		
CH_4	49.3	40.5	16.6	59.6	16.4	40.5	45.7	44.5	14.2	50.6	43.7	24.5	48.3	52.9	27.7	24.9	65.9	49.1
C_2H_6	2.0	0.2	-	0.2	-	-	1.3	-	-	-	0.6	-	-	1.2	-	-	0.4	0.8
C_2H_4	12.1	6.7	0.6	1.6	0.4	1.1	16.6	5.5	2.2	6.3	14.6	3.3	1.7	14.9	2.9	1.3	5.0	14.4
C_2H_2	2.2	3.3	4.4	2.1	2.7	2.8	1.3	1.4	3.0	3.0	3.5	5.7	3.0	1.6	5.4	4.4	1.4	3.0
C_3H_6	-	-	-	-	-	-	-	-	-	-	-	-	-	0.5	-	-	-	-
H_2	31.2	46.5	76.2	31.1	76.7	50.9	32.7	45.1	78.1	36.6	35.4	64.7	42.6	25.8	61.6	65.7	22.2	29.8
N_2	3.2	2.8	2.2	5.4	3.8	4.7	2.2	3.5	2.5	3.5	2.2	1.8	4.4	3.1	2.4	3.7	5.1	2.9
Carbon Black Formed (Mols/Mol Feed)	0.192	0.385	0.821	0.145	0.585	0.282	0.481	0.441	0.921	0.370	0.496	1.036	0.302	0.293	0.798	0.501	0.136	0.314

TABLE 3 - MATERIAL BALANCES - TESTS IN CIRCULAR REACTOR TUBE

RUN NO.	MOLS FEED/100 MOLS FEED GAS				MOLS PRODUCT/100 MOLS FEED GAS								NET MOLS FORMED/100 MOLS FEED GAS								
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_6	C_4H_{10}	H_2	C	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_3H_6	C_4H_{10}	H_2	C
Space Velocity = 15 Sec.$^{-1}$																					
7	91.	2.	0.5	-	61.9	-	1.3	2.7	-	-	60.5	26.6	-29.1	-2.0	1.3	2.7	-0.5	-	-	60.5	26.6
13	86.1	1.9	0.5	5.3	58.6	-	3.0	4.5	-	-	78.5	39.	-27.5	-1.9	3.0	4.5	-0.5	-	5.3	78.5	39.0
12	77.	1.7	0.4	15.4	68.7	0.3	6.4	7.0	-	-	79.6	46.7	- 8.3	-1.4	6.4	7.0	-0.4	-	-15.4	79.6	46.7
16	67.4	1.5	0.4	25.9	77.5	0.2	12.3	7.6	-	-	84.2	58.0	10.1	-1.3	12.3	7.6	-0.4	-	-25.9	84.2	58.0
24	58.1	1.3	0.3	36.4	78.7	0.4	24.6	9.9	-	-	83.8	57.4	20.6	-0.9	24.6	9.9	-0.3	-	-36.1	83.8	57.4
Space Velocity = 25 Sec.$^{-1}$																					
3	91.	2	0.5	-	78.	0.1	2.3	1.7	-	-	27.2	10.3	-13.0	-1.9	2.3	1.7	-0.5	-	-	27.2	10.3
15	86.2	1.9	0.5	5.2	78.6	0.6	6.3	2.5	-	-	31.6	14.8	- 7.6	-1.3	6.3	2.5	-0.5	-	-5.2	31.6	14.8
9	76.4	1.7	0.4	16.	82.1	0.7	15.7	3.6	-	-	36.4	21.8	5.7	-1.0	15.3	3.6	-0.4	-	-16.0	36.4	21.8
23	67.6	1.5	0.4	25.7	85.0	1.6	23.0	5.0	-	-	43.3	30.4	17.4	0.1	23.0	5.0	-0.4	-	-25.7	43.3	30.4
11	58.2	1.3	0.3	36.	84.6	1.7	31.5	5.3	2.6	2.6	38.5	26.5	26.4	0.4	31.5	5.3	-0.3	2.6	-33.4	38.5	26.5
Space Velocity = 35 Sec.$^{-1}$																					
4	91.0	2.0	0.5	-	80.3	0.1	2.3	1.7	-	-	22.9	8.0	-10.7	-1.9	2.3	1.7	-0.5	-	-	22.9	8.0
20	91.0	2.0	0.5	-	81.5	0.9	3.9	0.7	-	-	15.6	3.7	- 9.5	-1.1	3.9	0.7	-0.5	-	-	15.6	3.7
8	86.1	1.9	0.5	5.3	84.9	1.2	6.7	1.9	-	-	17.1	6.2	- 1.2	-0.7	6.7	1.9	-0.5	-	- 5.3	17.1	8.0
22	86.1	1.9	0.5	5.3	84.6	1.2	6.2	1.8	-	-	18.9	9.7	- 1.5	-0.7	6.2	1.8	-0.5	-	- 5.3	18.9	9.7
21	76.7	1.7	0.4	15.7	82.2	1.1	14.6	4.2	1.4	1.0	26.6	13.3	5.5	-0.6	14.6	4.2	-0.4	1.4	-14.7	26.6	13.3
10	67.7	1.5	0.4	25.6	82.0	1.4	16.5	2.8	1.4	7.2	25.3	17.7	14.3	-0.1	16.5	2.8	-0.4	1.4	-18.4	25.3	17.7
14	58.5	1.3	0.3	35.7	77.2	3.0	21.2	3.9	2.2	12.1	24.2	16.4	18.7	1.7	21.2	3.9	-0.3	2.2	-23.6	24.2	16.4

TABLE 4 - MATERIAL BALANCES - TESTS IN ANNULAR REACTOR TUBE

RUN NO.	MOLS FEED/100 MOLS FEED GAS				MOLS PRODUCT/100 MOLS FEED GAS								NET MOLS FORMED/100 MOLS FEED GAS								
	CH_4	C_2H_6	C_3H_8	C_4H_{10}	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_6	C_4H_{10}	H_2	C	CH_4	C_2H_6	C_2H_4	C_2H_2	C_3H_8	C_3H_6	C_4H_{10}	H_2	C
							Space Velocity = 15 Sec.$^{-1}$														
31	91.0	2.0	0.5	-	27.6	-	0.7	4.5	-	-	129.9	58.5	-63.4	-2.0	0.7	4.5	-0.5	-	-	128.9	58.5
43	86.4	1.9	0.5	5.0	41.8	-	2.2	7.4	-	-	110.2	50.1	-44.6	-1.9	2.2	7.4	-0.5	-	-5.0	110.2	50.1
36	76.8	1.7	0.4	15.6	29.7	-	4.6	6.3	-	-	163.5	92.1	-47.1	-1.7	4.6	6.3	-0.4	-	-15.6	163.5	92.1
42	68.1	1.5	0.4	25.1	57.9	-	6.1	11.3	-	-	129.0	79.8	-10.2	-1.5	6.1	11.3	-0.4	-	-25.1	129.0	79.8
39	58.4	1.3	0.3	35.8	58.5	-	7.9	13.6	-	-	154.6	103.6	0.1	-1.3	7.9	13.6	-0.3	-	-35.8	154.6	103.6
							Space Velocity = 25 Sec.$^{-1}$														
32	91.0	2.0	0.5	-	56.2	-	1.5	3.9	-	-	70.6	28.2	-34.8	-2.0	1.5	3.9	-0.5	-	-	70.6	28.2
40	86.2	1.9	0.5	5.2	68.4	-	2.4	4.3	-	-	60.4	30.2	-17.8	-1.9	2.4	4.3	-0.5	-	- 5.2	60.4	30.2
35	76.9	1.7	0.4	15.5	71.4	-	8.6	2.2	-	-	70.8	51.8	- 5.5	-1.7	8.6	2.2	-0.4	-	-15.5	70.8	51.8
45	68.2	1.5	0.4	25.0	81.0	1.3	23.7	5.0	-	-	49.1	31.4	12.8	-0.2	23.7	5.0	-0.4	-	-25.0	49.1	31.4
38	58.8	1.3	0.3	35.4	83.3	1.1	27.8	6.7	-	-	67.4	49.6	24.5	-0.2	27.8	6.7	-0.3	-	-35.4	67.4	49.6
							Space Velocity = 35 Sec. $^{-1}$														
30	91.0	2.0	0.5	-	72.5	0.2	1.9	2.6	-	-	37.8	14.5	-18.5	-1.8	1.9	2.6	-0.5	-	-	37.8	14.5
44	86.3	1.9	0.5	5.1	81.5	0.5	6.2	1.7	-	-	27.4	13.6	- 4.8	-1.4	6.2	1.7	-0.5	-	- 5.1	27.4	13.6
37	76.3	1.7	0.4	16.1	79.1	-	9.9	4.7	-	-	57.2	37.0	2.8	-1.7	9.9	4.7	-0.4	-	-16.1	57.2	37.0
41	68.2	1.5	0.4	25.0	84.3	1.9	23.7	2.6	0.8	-	41.1	29.3	16.1	0.4	23.7	2.6	-0.4	0.8	-25.0	41.1	29.3
34	58.9	1.3	0.3	35.3	84.1	2.4	30.5	2.8		-	60.1	48.1	25.2	1.1	30.5	2.8	-0.3		-35.3	60.1	48.1

TABLE 5

PRODUCT YIELDS - RICH GAS FEED

Run No.	Space Velocity	Feed Composition (Mols/100 Mols Feed)				Product Composition (Mols/100 Mols Feed)					
		CH_4	C_2H_6	C_3H_8	C_4H_{10}	CH_4	C_2H_6	C_2H_4	C_2H_2	H_2	C
		CIRCULAR REACTOR TUBE									
25	12.0	69.5	14.5	9.0	2.5	58.4	-	5.4	9.1	101.4	51.6
18	20.3	69.5	14.5	9.0	2.5	69.7	0.7	14.6	6.1	54.1	22.7
17	28.9	69.5	14.5	9.0	2.5	74.5	4.5	17.1	4.5	30.5	9.2
		ANNULAR REACTOR TUBE									
29	12.5	69.5	14.5	9.0	2.5	33.4	-	1.2	8.8	153.0	82.1
28	21.6	69.5	14.5	9.0	2.5	64.5	0.3	10.7	5.3	74.1	38.5
27	30.4	69.5	14.5	9.0	2.5	70.0	2.8	17.2	3.1	44.3	19.2

CALCULATION OF

$C_2H_4 - C_2H_2$ EQUILIBRIUM

$$C_2H_4 = C_2H_2 + H_2$$

$\Delta F^o = -R\,T \ln K_p$ R = 1.987 Btu/lb mol °R

Temp (°F)	Temp (°R)	ΔF^o (M Btu)*	$\ln K_p$	K_p
1600	2060	14.0	4093	0.033
1800	2260	7.7	4491	0.180
2000	2460	1.3	4888	0.767
2200	2660	-5.0	5285	2.56
2400	2860	-11.3	5683	7.31

*Free energy data were obtained from Rossini (1)

$$K_p = \frac{(p\ C_2H_2)(pH_2)}{(p\ C_2H_4)} \qquad \frac{p\ C_2H_2}{p\ C_2H_4} = \frac{K_p}{p\ H_2}$$

C_2H_2/C_2H_4 RATIOS

Temp (°F)	pH_2=0.05	pH_2=0.1	pH_2=0.2	pH_2=0.3	pH_2=0.4	pH_2=0.5	pH_2=0.6
1600	0.66	0.33	0.165	0.11	0.083	0.066	0.055
1800	3.60	1.80	0.90	0.60	0.45	0.36	0.30
2000	15.34	7.67	3.84	2.56	1.92	1.53	1.28
2200	51.50	25.75	12.87	8.58	6.44	5.15	4.29
2400	146.2	73.1	36.5	24.4	18.3	14.6	12.2

CALCULATION OF

$CH_4 - C_2H_2$ EQUILIBRIUM

$$2\ CH_4 = C_2H_2 + 3\ H_2$$

$\Delta F^o = - R\ T \ln K_p$ $\qquad R = 1.987$ Btu/lb mol °R

Temp (°F)	Temp (°R)	ΔF^o(MBtu)*	ln K_p	K_p
1600	2060	39.5	-9.64	6.6×10^{-5}
1800	2260	26.4	-5.88	2.8×10^{-3}
2000	2460	13.2	-2.70	6.7×10^{-2}
2200	2660	0.8	-0.151	8.6×10^{-1}
2400	2860	-12.2	2.15	8.56

*Free energy data were obtained from Rossini (1)

$$K_p = \frac{(p\ C_2H_2)\ (pH_2)^3}{(p\ CH_4)^2} \qquad \frac{p\ C_2H_2}{p\ CH_4} = \frac{K_p\ (p\ CH_4)}{(p\ H_2)^3}$$

SAMPLE CALCULATION - $T = 2000°F$ $\quad p\ CH_4 = 0.6 \quad K_p = 0.067$

pH_2	$(p\ H_2)^3$	C_2H_2/CH_4 Ratio
0.1	1×10^{-3}	40.4
0.3	2.7×10^{-2}	1.49
0.5	1.25×10^{-1}	0.323
0.7	3.43×10^{-1}	0.118

TABLE 6

CALCULATED EQUILIBRIUM TEMPERATURES

Tests in Circular Reactor Tube

Run No.	Space Velocity	% Butane in Feed	Gas Temperature from C_2H_2/C_2H_4 Equil.	Gas Temperature from C_2H_2/CH_4 Equil.
7	15	0	2020	1850
13	15	5	2000	1930
12	15	15	1940	1930
16	15	25	1850	1920
24	15	35	1790	1920
3	25	0	1800	1680
15	25	5	1720	1720
9	25	15	1650	1740
23	25	25	1660	1790
11	25	35	1620	1750
4	35	0	1770	1650
20	35	0	1590	1580
8	35	5	1620	1610
22	35	5	1630	1620
21	35	15	1650	1700
10	35	25	1590	1670
14	35	35	1580	1670
25	12	Rich Gas Feed	2030	2030
18	20		1780	1870
17	29		1660	1740

TABLE 7

CALCULATED EQUILIBRIUM TEMPERATURES

Tests in Annular Reactor Tube

Run No.	Space Velocity	% Butane in Feed	Gas Temperature from C_2H_2/C_2H_4 Equil.	Gas Temperature from C_2H_2/CH_4 Equil.
31	15	0	2320	2100
43	15	5	2170	2070
36	15	15	2050	2150
42	15	25	2060	2050
39	15	35	2050	2080
32	25	0	2080	1920
40	25	5	1990	1860
35	25	15	1750	1840
45	25	25	1670	1810
38	25	35	1710	1850
30	35	0	1910	1760
44	35	5	1660	1630
37	35	15	1800	1840
41	35	25	1590	1740
34	35	35	1580	1780
29	12	Rich	2350	2180
28	21	Gas	1830	1910
27	30	Feed	1660	1800

GAS TEMPERATURE ESTIMATION FROM HEAT TRANSFER CONSIDERATIONS

a) Proposed Mechanism

The heat transfer to the reacting gases was considered to take place mainly by radiation from the tube wall to a cloud of carbon particles at or very near to thermal equilibrium with the gas. The heat transferred by convection from the tube wall to the gas was also taken into account.

b) Outline of Calculations

1) A final gas temperature was assumed and the sensible and reaction heat loads calculated.

2) The temperature drop through the tube wall and hence the inside wall temperature for this heat load were calculated.

3) The area required for sensible heat transfer was calculated using the log mean temperature difference.

4) The final gas temperature was calculated from the remaining area and the heat of reaction.

5) If the calculated gas temperature did not agree with the assumed gas temperature the calculation was repeated.

c) Estimates and Assumptions

1) The convection heat transfer coefficients were estimated as:

Space Velocity (sec^{-1})	15	25	35
h_c (Btu/hr. ft^2 °F)	8	12	16

2) The assumed emmissivity values were

Silicon carbide tube wall - $\epsilon_1 = 0.85$

Carbon particles - $\epsilon_G = 0.9$

3) The heat of reaction was assumed to be constant over the temperature range involved.

4) View factor = 1

5) An average reactor tube temperature was used in the calculations although the tube's temperature will vary slightly along its length.

d) Reactor Tube Data

	Circular Tube (1-1/8" Inside Diameter)	Annular Tube (2" x 1-5/8" Annulus)
Length (inches)	30	30
Inside Wall Area (ft^2)	0.761	1.31
Outside Wall Area (ft^2)	1.227	1.80
Log Mean Wall Area (ft^2)	0.961	1.555
Wall Thickness (inches)	3/8	3/8
Thermal Conductivity* (Btu in/hr. ft^2 °F)	109	67

*Manufacturer's Data.

e) Sample Calculation

EXAMPLE - Circular reactor tube

Space velocity = 35

% Butane in feed = 35

(1) Calculation of Heat Effects

Overall enthalpy change for 1 mol of feed at 77°F to product at 2000°F

	FEED		PRODUCT	
	Mols	Enthalpy[1] at 77°F	Mols	Enthalpy at 2000°F
CH_4	0.585	-18.90	0.772	-2.78
C_2H_6	0.013	- 0.47	0.030	3.72
C_2H_4	-		0.212	12.85
C_2H_2	-		0.039	4.91
C_3H_8	0.003	-0.13	-	
C_3H_6	-		0.022	1.46
C_4H_{10}	0.357	-19.10	0.121	4.53
H_2	-		0.242	3.34
N_2	0.042	0	0.042	0.60
C	-		0.164	1.42
TOTAL	1.000	-38.60	1.644	30.05

1. Basis: C as graphite at 77°F H_2 as gas at 77°F
N_2 as gas at 77°F

Total Entahlpy change	=	68.65 M Btu/mol
Sensible Heat to 2000°F	=	51.05 M Btu/mol
Heat of Reaction at 2000°F		17.6 M Btu/mol

Assume that the heat of reaction is constant over the temperature range involved in the calculations.

Assume final gas temperature = 1600°F

Feed rate = 1.117 mols/hr.

Sensible Heat to 1600°F	=	38.0 M Btu/mol	=	42.5 M Btu/hr
Reaction Heat	=	17.6 M Btu/mol	=	19.7 M Btu/hr
TOTAL	=	55.6 M Btu/mol	=	62.2 M Btu/hr.

2. Temperature Drop Through Tube Wall

Conduction equation: $\Delta t = \frac{q \Delta l}{kA}$

A for conduction = log mean area = 0.961 ft^2

$k = 109$ Btu/in./hr. ft^2 °F

$\Delta l = 3/8$ inch

$q = 62,200$ Btu/hr.

$$\Delta t = \frac{(62,200)(3/8)}{(109)(0.961)} = 220^{\circ}F$$

Outside tube temperature $(T_o) = 2550^{\circ}F$

Inside tube temperature $(T_1) = 2550 - 220 = 2330^{\circ}F = 2790^{\circ}R$

3. Sensible Heat Transfer

$$q = h_c A\Delta t + A\sigma \left[\frac{1}{(1/\epsilon_1 + 1/\epsilon_G - 1)}\right]\left[\left(\frac{T_1}{100}\right)^4 - \left(\frac{T_G}{100}\right)^4\right] = 42500 \text{ Btu/hr.}$$

$$\text{log mean } \Delta t = \frac{\Delta t_1 - \Delta t_2}{\ln \Delta t_1/\Delta t_2} = \frac{2253 - 730}{\ln 2253/730} = 1330^\circ\text{F}$$

$$T_G = 2330 - 1330 = 1000^\circ\text{F} = 1460^\circ\text{R.}$$

NOTE

The use of the log mean temperature as the average gas temperature for radiation calculations is probably not strictly correct, but the total radiatn heat transfer will be so insensitive to changes in the gas temperature that the resulting error should be negligible.

$$\epsilon_1 = 0.85 \qquad \epsilon_G = 0.9 \qquad \frac{1}{1/\epsilon_1 + 1/\epsilon_G - 1} = 0.775$$

$\sigma = 0.1713$ Btu/hr. ft^2 $^\circ$R^4

$h_c = 16$ Btu/hr. ft^2 $^\circ$F

Solving

$A = 0.444$ ft^2 for sensible heat transfer.

4. Reaction Heat Transfer

$$q = h_c A \Delta t + A \sigma \left[\frac{1}{1/\epsilon_1 + 1/\epsilon_G - 1} \right] \left[\left(\frac{T_1}{100}\right)^4 - \left(\frac{T_G}{100}\right)^4 \right]$$

$$= 19,700 \text{ Btu/hr.}$$

Using assumed value of $T_G = 1600^\circ F$ $\Delta t = 730^\circ F$

Solving: $T_G = 2070^\circ R = 1610^\circ F$

Assumed $T_G = 1600$

$\therefore$ Recalculation unnecessary.

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